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RESEARCH ON THE ELECTRO-  
CHEMICAL OXIDATION OF  
HEXANE AND ITS ISOMERS

Sixth Semiannual Interim Report

Covering Period

May 16 - November 15, 1968

Contract No. DA 44-009-AMC-1408(T)

Prepared by

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Prepared for

U. S. Army Mobility Equipment  
Research and Development  
Center  
Fort Belvoir, Virginia

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### ABSTRACT

The oxidation of  $\text{CH}_4$  on Pt electrodes in 80%  $\text{H}_3\text{PO}_4$  has been studied at 110 and 130°C. Particular emphasis has been placed on possible methods of developing non-noble metal catalysts. The difficulties associated with this development, in particular corrosion, are discussed. A possible method of overcoming these difficulties and of stabilizing non-noble methods is described, involving their adsorption in submonolayer quantities.

A study of Cu adsorbed on both smooth and platinized Pt has been made. In presence of  $\text{Cu}^{++}$ , Cu is adsorbed onto Pt at a rate limited by  $\text{Cu}^{++}$  diffusion. Steady-state coverage is high and the isotherm is very similar to isotherms found for typical organic species; there is high coverage at low potentials ( $\leq 0.3$  v vs. RHE) and a decrease in coverage at higher potentials. The coverage becomes zero above 0.7 v. The relationship between the charge to oxidize the Cu layer,  $Q$ , and its coverage,  $\theta$ , allows calculation of the number of electrons released per site when the layer is oxidized,  $[e]$ . For Cu at 130°C,  $[e]$  is 1 electron/site, i.e. indistinguishable from O-type hydrocarbons. An  $[e]$  value of 1 electron/site would correspond to a layer where the Cu atoms occupy two Pt surface sites. At 110°C the Cu layer releases about 1.8 electrons/site on oxidation, indicating that each Cu atom occupies one Pt site.

Cu adsorbs less rapidly in presence of  $\text{CH}_4$ , than in its absence. The evidence for this is that while the rate of adsorption of the combined layer, in presence of both  $\text{CH}_4$  and  $\text{Cu}^{++}$ , is higher than in presence of either  $\text{CH}_4$  or  $\text{Cu}^{++}$  alone, it is slower than the sum of the rates of adsorption of the two components. In the steady state, both the coverage and the charge to oxidize the adsorbed layer are higher in presence of both  $\text{Cu}^{++}$  and  $\text{CH}_4$  than in presence of either component alone. However, coverage or charge is lower than their respective sums for Cu and  $\text{CH}_4$  alone.

The charge vs. coverage plots in presence of adsorbed Cu and  $\text{CH}_4$  are slightly different than for the individual components; in

the middle range of coverage the plot for the combined layer departs from linearity and invariably shows less oxidizable charge than anticipated. There is also a slight difference in the average oxidation state of the various adsorbed layers in the steady state. Thus, for adsorption at potentials below 0.4 v,  $\text{CH}_4$  releases about 1.25 electrons/site on oxidation and the combined layer releases about 1.4 electrons/site. Above 0.4 v, both the Cu and the Cu +  $\text{CH}_4$  layers show a sharp increase in the average oxidation state of the adsorbed layer.

There is a distinct difference in behavior between Cu and the Cu +  $\text{CH}_4$  combined layer with respect to behavior on open circuit after formation. When an electrode with a Cu layer is open circuited, its potential rises to about 0.94 v, with a sloping arrest in the region of 0.55 v. The behavior of an electrode with a Cu +  $\text{CH}_4$  layer depends on its potential of formation. In all cases the final potential is  $0.40 \pm 0.01$  v. For adsorption above 0.4 v, the potential first moves to lower values, during which increasing adsorption occurs at open circuit. For adsorption potentials below 0.4 v, there is a uniform increase to 0.4 v on open circuit. The shapes of these transients are determined by equal anodic and cathodic reactions involving  $\text{Cu}^{++}$  deposition and O-type  $\text{CH}_4$  formation and oxidation. A quantitative analysis of the contributions of these individual reactions is not possible, however, and a special cell is described in which it is possible to form the inorganic and organic layers separately and quantitatively and to study the effects of the inorganic layer on the properties of the adsorbed layer.

On platinized Pt the charge to oxidize the combined Cu +  $\text{CH}_4$  layer is considerably greater than the corresponding charge for pure  $\text{CH}_4$ . The over-all oxidation rate of  $\text{CH}_4$  is inhibited in presence of  $\text{Cu}^{++}$  and concentrations of  $\text{Cu}^{++}$  as low as 60 parts per billion significantly decrease the hydrocarbon oxidation rate. It is shown

that this inhibition arises substantially from the inhibition of the rate-limiting step of the  $\text{CH}_4$  oxidation reaction, i. e. the oxidation of O-type to  $\text{CO}_2$ .

The DA Project/Task Area/Work Unit Number assigned to this contract is 1T061102A34 00 009 EF.

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## **I. PRESENT STATUS OF THE MECHANISM OF HYDROCARBON OXIDATION ON Pt**

In studies carried out previously, we have explored the mechanism of the anodic oxidation of the hydrocarbons  $\text{CH}_4$ <sup>(1, 7)</sup>,  $\text{C}_3\text{H}_8$ <sup>(1-4)</sup>, and  $n\text{-C}_6\text{H}_{14}$ <sup>(5)</sup> on Pt electrodes in hot (130°C) concentrated (80 wt %)  $\text{H}_3\text{PO}_4$ . The following is a brief summary of our conclusions based on previous observations:

(1) The reaction must occur by means of adsorption, and all intermediates between the hydrocarbon reactant and the product ( $\text{CO}_2$ ) are adsorbed on the electrode.

(2) When hydrocarbons adsorb on Pt electrodes, three adsorbed species are found. These are the CH- $\alpha$ , CH- $\beta$  and O-type residues.

(3) The CH- $\alpha$  material can be hydrogenated. It is therefore assumed to be an alkyl group or a partially hydrogenated alkyl group. Gas chromatographic analysis of the effluent after hydrogenation of the CH- $\alpha$  material shows that some C-C bond breaking has occurred<sup>(12)</sup>. The amount of CH- $\alpha$  increases with increasing molecular weight of the hydrocarbon. Thus, there is no CH- $\alpha$  with  $\text{CH}_4$ , but it contributes about half of the charge for the adsorbate of  $n\text{-C}_6\text{H}_{14}$ <sup>(5)</sup>. In the case of  $\text{C}_3\text{H}_8$ , a composition of somewhere between  $\text{>C}$  and  $\text{>CH}$  has been suggested to correspond to the CH- $\alpha$  material at low potentials<sup>(1)</sup>.

(4) The CH- $\beta$  material is not cathodically desorbable by hydrogenation. It is unreactive towards oxidation and its amount increases from  $\text{CH}_4$  to  $n\text{-C}_6\text{H}_{14}$ . Its oxidation state is such as to suggest that most of the original CH bonds of the hydrocarbon have not been replaced by CO bonds: it may be a carbonaceous polymer.

(5) The major constituent of the adsorbed layer in terms of coverage is O-type. O-type is found for all hydrocarbons thus far investigated and appears identical<sup>(6)</sup> with the species reported

by Giner<sup>(8, 9)</sup> "reduced CO<sub>2</sub>." Its oxidation state and the fact that it cannot be hydrogenated, suggest that it contains oxygen. Based on results with methane<sup>(1)</sup>, a composition  $\geq C(OH)$  was suggested.

(6) We have shown that the oxidation of O-type to CO<sub>2</sub> is the rate limiting step at low potentials (certainly for potentials  $\leq 0.35$  v vs. RHE) for the oxidation of CH<sub>4</sub><sup>(1)</sup> and C<sub>3</sub>H<sub>8</sub><sup>(1, 10)</sup> and probably for a range of higher hydrocarbons. The over-all scheme we have suggested for C<sub>3</sub>H<sub>8</sub><sup>(1)</sup> is



The oxidation of O-type probably occurs by participation of H<sub>2</sub>O molecules adsorbed on bare sites on the electrode and we have shown that the presence of CH- $\alpha$  on these sites inhibits O-type oxidation<sup>(1, 10)</sup>; similarly, lowering the water concentration in the solvent inhibits the reaction.

(7) At higher potentials (e.g. 0.5 v) the above mechanism does not operate. The slow step becomes the initial adsorption process itself and the adsorbate reacts to form CO<sub>2</sub>. The reaction probably does not proceed via O-type in this case, however.

A number of important aspects of the reaction mechanism remain to be resolved: e.g. (a) the quantitative definition of the role of water in the oxidation of O-type and a decision as to whether the reacting H<sub>2</sub>O has to be adsorbed on the electrode, and (b) the chemical structure of the important CH- $\alpha$  species. Since it appears that CH- $\alpha$  oxidation becomes rate limiting with higher molecular weight hydrocarbons, this would become more important with those compounds.

It is clear that there is much more about the reaction which we need to know for an adequate understanding of its mechanism. For all this, however, our understanding of the reaction is now at a sufficiently advanced stage that we can begin to see how to use

our knowledge in catalyst development. The most important immediate requirement in hydrocarbon fuel cell technology is to find some way to break away from noble metal catalysts-- which are expensive and rare. Correspondingly, we consider this an appropriate stage in our program to attempt to use our mechanistic understanding as a guide in catalyst development. Our approach to the possible development of non-noble metal hydrocarbon fuel cell catalysts is described in the next section.

## **II. NON-NOBLE CATALYSTS FOR HYDROCARBON OXIDATION**

It has been found that hydrocarbon oxidation in aqueous systems only readily occurs in strongly acid environments<sup>(11, 12)</sup>. This is fortunate from the point of view of CO<sub>2</sub> rejection, but causes severe corrosion problems. Because of the corrosive environment, one commonly only considers the use of noble metal catalysts. These are excellent catalysts for reactions involving adsorbing hydrocarbons<sup>(13)</sup> but, almost by definition, are expensive and rare. It has been demonstrated that Pt shows the best activity of any of the noble metals<sup>(14)</sup> (although some minor improvements have been reported with Pt-Ru alloys<sup>(15)</sup>). Considering its cost and rarity, however, the use of Pt catalysts on a wide scale is not attractive.

It would be far better to use non-noble metals but, as we have explained, such use is precluded because of corrosion. A possible way to stabilize a non-noble metal would be to compound it. In the absence of a passive film, though, one would not expect to achieve great stabilization by forming intermetallic compounds, since their free energies of formation are often small<sup>(16)</sup>. In any case, one is somewhat reluctant to attempt to make the compounds blindly, with no evidence of their usefulness, because of experimental difficulties. In addition, one might say that such intermetallic compounds (noble-non-noble metals) usually have an oxide film on them. Corrosion stability conferred on a compound by a passive oxide film would not be desirable since it is probable that potential drops in the oxide would mitigate against usefulness as a hydrocarbon oxidation catalyst. Therefore, an alternative method of stabilizing possible non-noble metal catalysts is required.

Another possibility for the stabilization of non-noble metals is to adsorb them on an inert substrate. Thus, in submonolayer amounts, reasonable heats of adsorption would allow the formation of layers which are stable at potentials well positive of the normal

expectations of bulk thermodynamics. We note that 23 kcal/mole of chemisorption energy, which is not a large amount for a chemisorbed layer<sup>(17)</sup>, would enhance stability by 1 v. This opens up a wide range of non-noble metals which can be used as possible hydrocarbon oxidation catalysts. For example, of the metals, we could suggest Zn, Cd, Hg, Cu, Ag, Ni, Co, Fe, Mo, W, Ga and In. For non-metals, possibilities such as P, S, As, Se and Te may be suggested. The notion is then that by adsorbing sub-monolayer amounts of the indicated materials, or others, it may be possible to stabilize a non-noble metal catalyst.

There is some evidence to suggest that this approach is valid. For example, there are a number of reports in the literature of "undervoltage" in metal deposition<sup>(18, 19)</sup>. Undervoltage is a phenomenon where metals are plated out at potentials positive to the reversible potential. The reason for this undervoltage is that below a monolayer the metal activity is less than 1 and for the reaction



the equilibrium potential, given by

$$E = E_0 + \frac{RT}{ZF} \ln \frac{a_{M^{+2}}}{a_M}, \quad (3)$$

becomes more positive as  $a_M$ , the activity of the metal decreases.

Specifically, one may note the recent results of Breiter<sup>(19)</sup> who was able to plate Cu onto Pt above the reversible potential for Cu deposition; equally important, he also noted the relative difficulty of removing this layer once it was formed. Similar observations for a number of elements have been reported<sup>(20, 21)</sup>. The possibility of plating S, Se and Te onto Pt electrodes was recently reported by Binder, et al.<sup>(22)</sup>. Closer to home we may

note the formation of oxides on Pt below the oxygen reversible potential and the presence of an adsorbed H atom layer above the  $H_2$ -reversible potential, both examples of adsorption stabilized films. It appears extremely probable, then, that we will be able to form and to maintain submonolayer amounts of non-noble metals on inert substrates.

This approach has not been tried before, and we do not have much direct evidence on the catalytic behavior of submonolayers. The reasons for exploring this approach have been indicated and there is much information in the general heterogeneous catalysis literature that suggests that many of the metals mentioned would be useful for C-H and C-C bond breaking. For example, in C-H bond breaking Ni, Co and Fe are active<sup>(23)</sup> as well as Pd, Pt, Rh and W. Also active in catalytic hydrogenolysis, are Fe, Co, Ni, Pt and W<sup>(24)</sup>. In catalytic reforming, Ru and Re are excellent<sup>(25)</sup> for inducing C-C bond breaking but are not used because they do not lead to much isomerization, probably an irrelevant consideration here. All of these metals would, if stable, assist reactions (1a and 1b) where they involve C-H or C-C bond breakings.

We assume here that the properties of the adsorbed submonolayer will approximate the properties of the metal in bulk. In support of this are the conclusions of Hayward and Trapnell<sup>(26)</sup>; they report that for the chemisorption of  $O_2$  on W, CO on Ni, and  $H_2$  on Ni, the heats of chemisorption are similar to the heats of formation (in the gas phase) of the compounds  $WO_3$ ,  $Ni(CO)_4$ , and  $NiH$ . To quote, this "suggests that chemisorption on metals is not dissimilar from chemical reactions of metal atoms in the gas phase." Also, "in chemisorption metal atoms are acting as isolated units." Again, "the surface properties of a metal may be determined as much by

the properties of the isolated atoms as by the properties of the metallic crystal." This view is perhaps rather extreme and would not be generally accepted<sup>(13)</sup>. The general notion is valid, however, and it is clear that the surface properties of an inert substrate can be modified via an adsorbed layer.

We have no evidence of the efficacy of the metals mentioned in catalyzing the addition of oxygen, as required in reactions (1b) and (1c). However, they may be good catalysts, particularly those metals which normally passivate readily. Also there are some indications in the literature that immediately suggest that this could be a fruitful line of attack. For example, the results of Binder, et al.<sup>(22)</sup>, show that adsorbed S, Se and Te catalyze the oxidation of formic acid and CO. Again, we may note the work of Shropshire<sup>(27)</sup> who appeared to find catalytic activity for the oxidation of methanol by adsorbed perrhenate and molybdate ions, although this does not appear to have been pursued. In another vein, Fleischmann, et al.<sup>(28)</sup>, have shown that electrodeposited Ru on Hg showed unusually high activity for H<sub>2</sub>-evolution, and they were able to show that this is due to an exceptionally high concentration of kink and step sites on the surface. These observations suggest the possibility that a deposit which has an extremely active morphology for catalysis can be obtained.

In summary, then, there is every indication that these layers can be formed and stabilized by adsorption, and there are significant indications that, once formed, reasonable catalytic activity can be obtained. Correspondingly, the major emphasis of our program has changed from a direct study of the reaction mechanism as such to an investigation of the stability and catalytic usefulness of non-noble metal adsorbed layers. Because our previous understanding of the hydrocarbon to CO<sub>2</sub> reaction was developed with Pt electrodes, our initial studies have been made with layers adsorbed on this "inert" substrate.



### III. ADSORPTION OF Cu ON SMOOTH Pt

In the first instance we have chosen to work with Cu because there is good evidence in the literature<sup>(19)</sup> that Cu is held adsorbed at potentials above its reversible potential. The Cu layer there is suitable for the development of experimental techniques for the study of these systems. In this section we describe the initial experiments on the adsorption of Cu on smooth Pt at 130°C.

The earlier evidence which shows that Cu can be adsorbed on Pt at potentials more positive than the  $\text{Cu}^{++}$  equilibrium<sup>(19)</sup> relates to room temperature. As the temperature increases, the stability of the layer should decrease and, while we do not know how the reversible potential for  $\text{Cu}^{++}/\text{Cu}$  varies with temperature, we can generally expect an adsorbed Cu layer to be less stable at 130°C than under ambient conditions. The adsorption of Cu on smooth Pt was therefore studied.

Experimentally, the procedure was basically as we have described previously<sup>(1)</sup>. Experiments were carried out in 80%  $\text{H}_3\text{PO}_4$  at 110 and 130°C, mostly the latter. The gases were suitably presaturated with water vapor. In most of the experiments, the electrolyte which had not been treated with  $\text{H}_2\text{O}_2$  was purified by adsorption. For this purpose, a large surface area fuel cell electrode was held at 0.3 v vs. reversible hydrogen electrode (RHE) for 24 hours with vigorous gas stirring. After this period, the electrode was removed from solution. After this treatment it was found that no measurable adsorption occurred on a smooth Pt electrode held at 0.3 v for 10 minutes with gas stirring. Correspondingly, there were no effects on our results from contamination.

Initially, in this study of Cu adsorption, we feared that Cu would plate onto our H<sub>2</sub>-reference electrode and spoil its reversibility. A number of experiments were therefore carried out to examine a working O<sub>2</sub>-electrode, which would not thus be contaminated, in place of the H<sub>2</sub>-electrode. Experimentally, the behavior of the O<sub>2</sub> electrode was found to be considerably less reproducible than the H<sub>2</sub> electrode, showing both short-term and long-term potential drifts. Correspondingly, we continued use of the dynamic H<sub>2</sub>-electrode<sup>(29)</sup>. To avoid possible irreversibility effects on the H<sub>2</sub>-reference electrode from adsorbed Cu, we regularly anodized it to oxidize any such adsorbed Cu. Since the reference electrode is platinized Pt and is in an unstirred compartment of the cell, this did not turn out to be as serious a problem as had been feared.

Most of our interest was in continuing to study reactions at 130°C. Since, however, we feared a lack of stability of the adsorbed layer at this temperature, some studies were made initially at 110°C. It turns out that temperature does not have a large effect in the range we have explored and that we can say with certainty that appropriate adsorbate coverages can be achieved at both 110 and 130°C with only quite minor Cu<sup>++</sup> concentrations in solution. Preliminary experiments were designed to explore the effect of measuring current density on the charge to oxidize the adsorbed layer. As we expected, the charge was independent of the measuring density in the range explored, 20 - 300 ma/r cm<sup>2</sup>. The rate of attainment of steady-state adsorption was controlled by diffusion of Cu<sup>++</sup> ions in solution, as we shall discuss in a little more detail later. Most of our experiments were done with stirring.

Figure 1 shows the charge to oxidize the steady-state layer adsorbed in presence of Cu<sup>++</sup> ions at 110 and 130°C. Following Breiter<sup>(19)</sup>, we will assume that the adsorbed layer is Cu metal

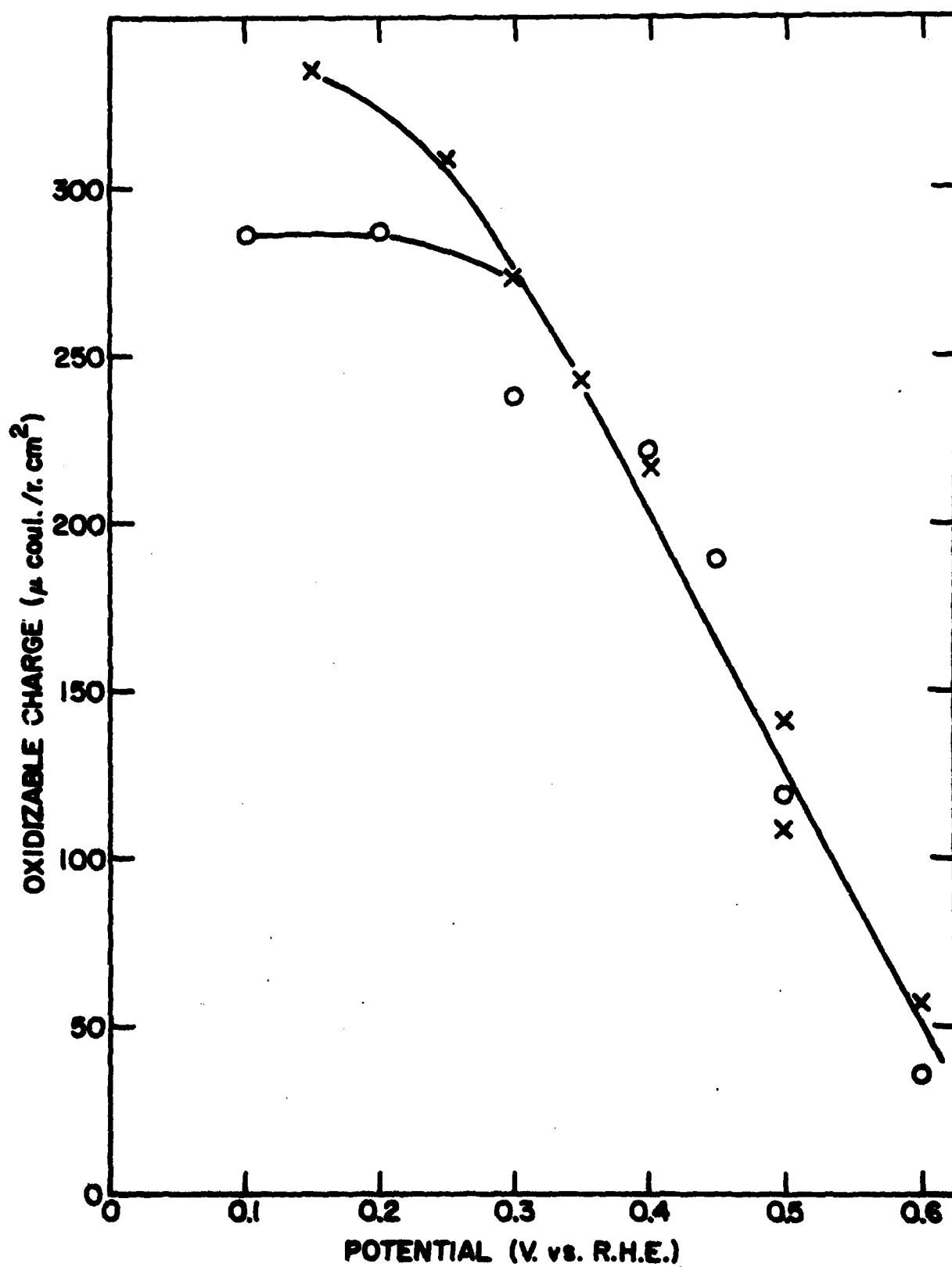


Fig. 1 Steady state adsorption of Cu on smooth Pt foil as a function of potential of adsorption (x, 110°C and  $3 \times 10^{-4}$  M  $\text{Cu}^{++}$ ; o, 130°C and  $2 \times 10^{-5}$  M  $\text{Cu}^{++}$ ).

and that the measured oxidation charge is for the process  $\text{Cu} \rightarrow \text{Cu}^{++} + e^-$ . The charges found are quite consistent with this assumption in that a maximum of about  $300 \mu\text{coul}/\text{r cm}^2$  is found. The figure shows an adsorption isotherm scarcely distinguishable from similar studies for adsorbed organic compounds. It is evident that there is appreciable adsorption at potentials as high as 0.6 v vs. RHE, and no doubt with higher  $\text{Cu}^{++}$  concentrations a higher coverage could be attained at these more positive potentials. The stability of the adsorbed layer is then sufficient for our purpose.

Figure 2 shows the coverage of the Pt electrode as measured by cathodic hydrogen charging. Again, the results are very similar to typical findings for organic adsorbed layers.

In Fig. 3 we show the relationship between the charge to oxidize the adsorbed Cu and its coverage. These experiments were carried out for the adsorbate at  $110^\circ\text{C}$  and the measurements were made by interrupting the adsorption process, which was carried out without stirring at various potentials. Results for the different potentials are essentially identical. We seem to find a single relationship between  $Q$  and  $\theta$ , passing through the origin, and with a slope of 1.8 electrons/site. This is what one might expect for the oxidation of adsorbed Cu to  $\text{Cu}^{++}$ , if the Cu were attached to a single site.

Results at  $130^\circ\text{C}$  were somewhat less simple to explain. The data are shown in Fig. 4. In this case, the relationship between  $Q$  and  $\theta$ , while linear and passing through the origin, has a different slope. Indeed, we find a slope of 1.05 electrons/site, quite typical of O-type adsorbed layers. This value is found for most of the adsorbate, although we have some indirect evidence that a higher  $[e]$  value is found during the latter stages of adsorption (i.e. the ratio of  $Q/\theta$  for the steady state layer; see Fig. 12). The finding of a major region in the  $Q/\theta$  plots with a slope of 1.05 was somewhat discouraging in that we had hoped to be able to distinguish adsorbed Cu from

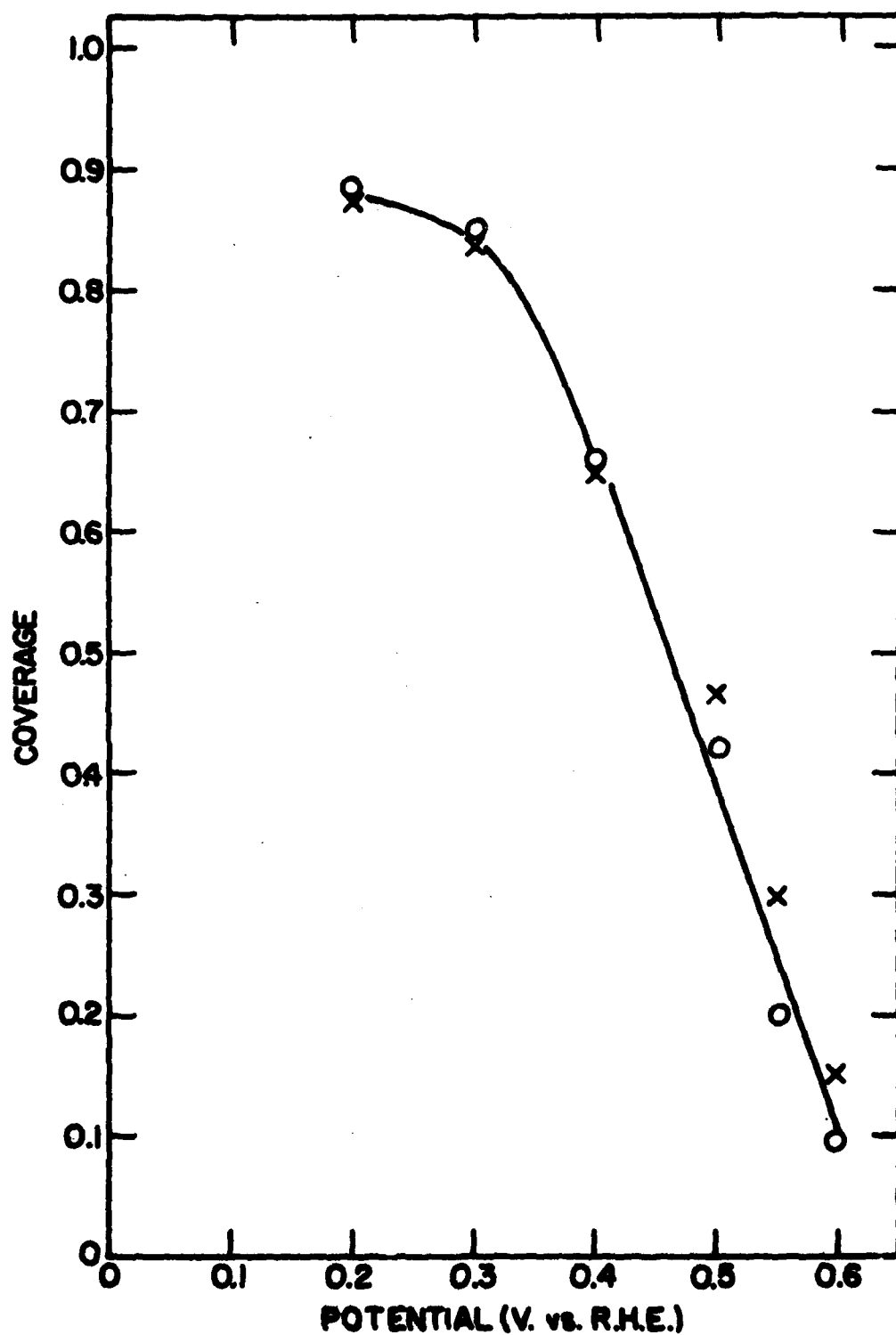


Fig. 2 Steady state coverage of Cu on smooth Pt foil as a function of potential of adsorption (x, 110°C and  $3 \times 10^{-4}$  M  $\text{Cu}^{++}$ ; o, 130°C and  $2 \times 10^{-5}$  M  $\text{Cu}^{++}$ ).

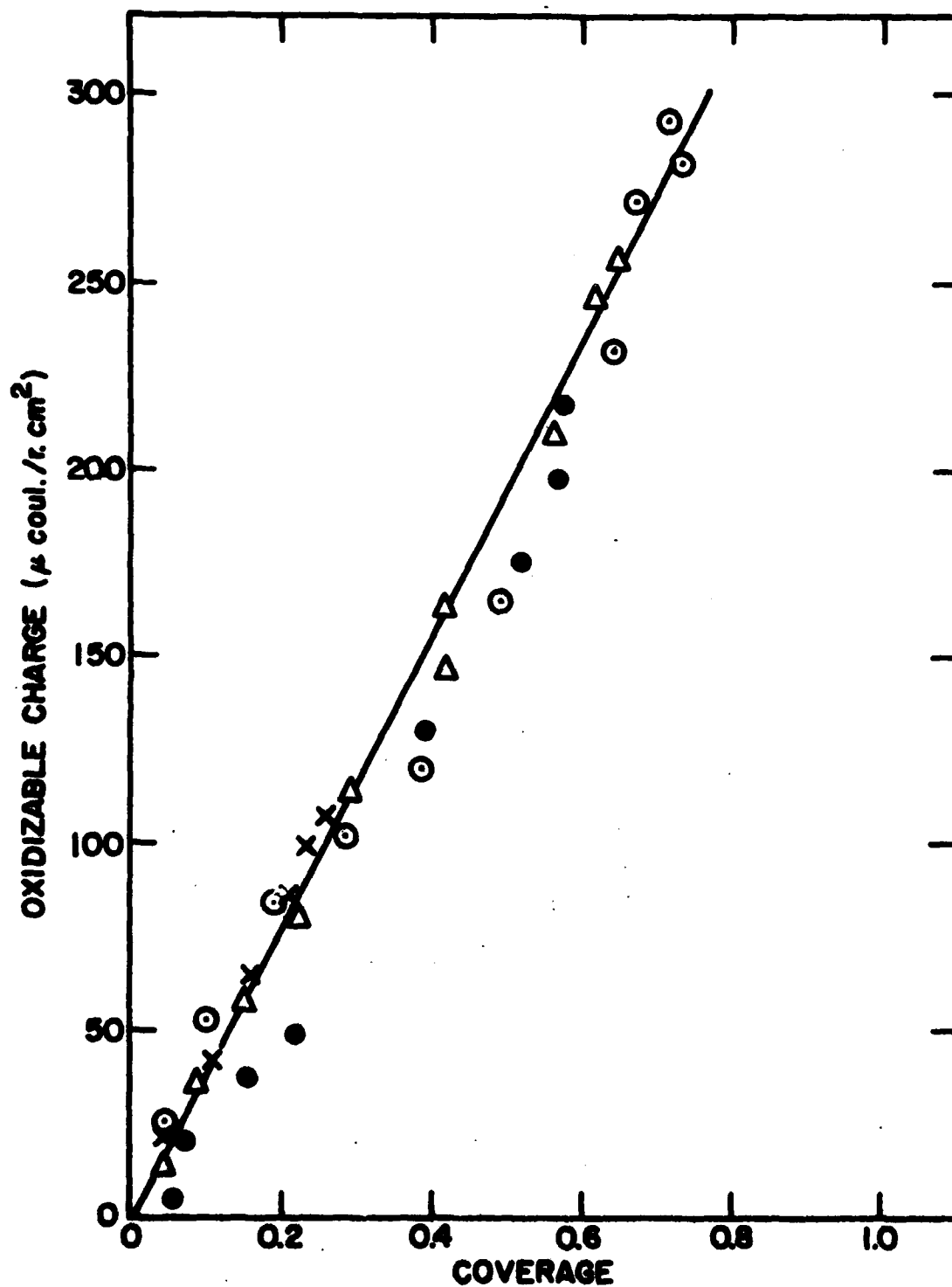


Fig. 3 Ratio of charge accumulation to coverage with Cu at 110°C as a function of potential during adsorption; ( $\Delta$ , 0.25 v;  $\odot$ , 0.30 v;  $\bullet$ , 0.40 v;  $\times$ , 0.50 v).

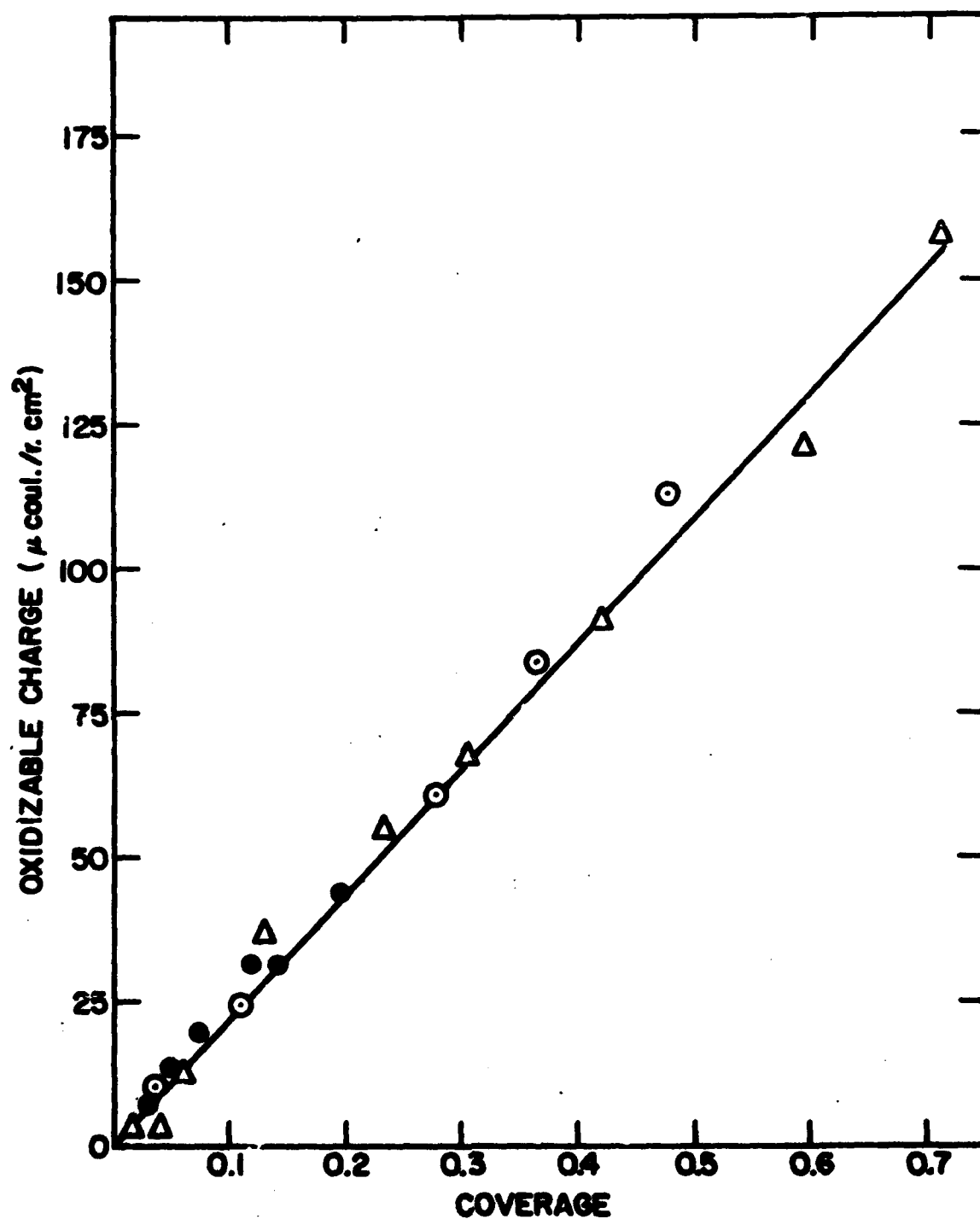


Fig. 4 Ratio of charge accumulation to coverage with Cu at 130°C, as a function of potential during adsorption; (Δ, 0.15 v; ⊙, 0.45 v; ●, 0.55 v).

adsorbed O-type hydrocarbons by measurement of the Q- $\theta$  relationship. This would not, of course, be possible under the present circumstances.

Another interesting sidelight of these results (Figs. 1, 2 and 4) is that they are almost identical with the results of similar experiments for O-type hydrocarbons and reduced CO<sub>2</sub>. This is somewhat disturbing since it raises some doubts concerning the previous identification of the O-type hydrocarbons as reduced CO<sub>2</sub> which was based on similarity of Q- $\theta$  plots.

The important point in the present context is that we have shown that adsorbed Cu is stable under our experimental conditions, and correspondingly, we have investigated the co-adsorption of Cu and CH<sub>4</sub>.



#### IV. CO-ADSORPTION OF Cu AND CH<sub>4</sub> ON SMOOTH Pt

The CH<sub>4</sub> system was chosen for study because of its simplicity<sup>(1,7)</sup>. Thus we could be sure that only one kind of adsorbed material is present on the electrode, namely O-type, and that any variations in  $Q_{ads}^{CH_4}$  would result from changes in the amount of O-type. Had we studied C<sub>3</sub>H<sub>8</sub> or n-C<sub>6</sub>H<sub>14</sub>, changes in  $Q_{ads}$  might have reflected different ratios of O-type and CH-type hydrocarbons.

Figure 5 shows the rate of adsorption with stirring of Cu and CH<sub>4</sub> at 130°C. In both cases the adsorption rate was limited by diffusion. The Cu<sup>++</sup> concentration ( $2 \times 10^{-5}$  M) was adjusted to make the rate of Cu adsorption about one-half the rate of CH<sub>4</sub> adsorption, as shown. In presence of both Cu and CH<sub>4</sub>, the adsorption rate was strongly affected by stirring but was somewhat slower than the combined rates for Cu and CH<sub>4</sub>. We had evidence to suggest that this is due to inhibition of Cu deposition by presence of adsorbed CH<sub>4</sub>. Thus, when CH<sub>4</sub> is flushed from solution, the subsequent rate of Cu deposition tended to be less than its diffusionally controlled rate until the very last traces of CH<sub>4</sub> had been removed.

Figure 6 compares the charge to oxidize adsorbed CH<sub>4</sub>, Cu and their combined layer at 130°C. We see that in presence of both solution species more oxidizable adsorbate is formed than for the individual species, particularly at more positive potentials. However, the combined  $Q_{ads}$  is always less than the sum of the charges found for the individual steady-state layers. Similar results are seen in Fig. 7 for the coverage of the electrode of the adsorbed layers.

In order to investigate the composition of the adsorbed layer, we have explored the  $Q-\theta$  plots during adsorption in presence of both CH<sub>4</sub> and Cu<sup>++</sup>. Results for various potentials of adsorption are shown in Figs. 8 - 11. Here, for comparison, we have shown data for CH<sub>4</sub>, Cu and the combined layer. The Cu and CH<sub>4</sub> results

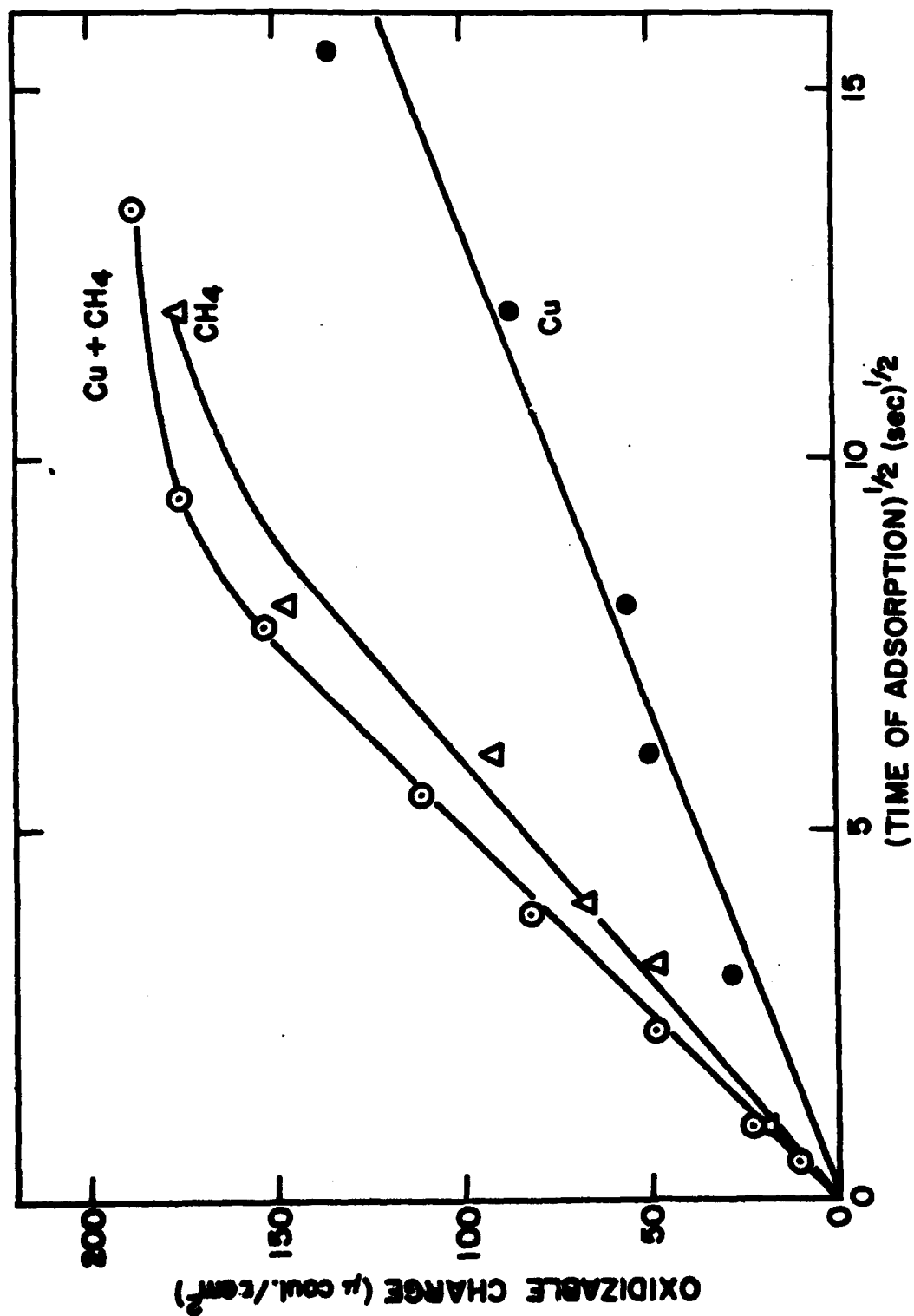


Fig. 5 Rate of charge accumulation as a function of time and material at 130°C.

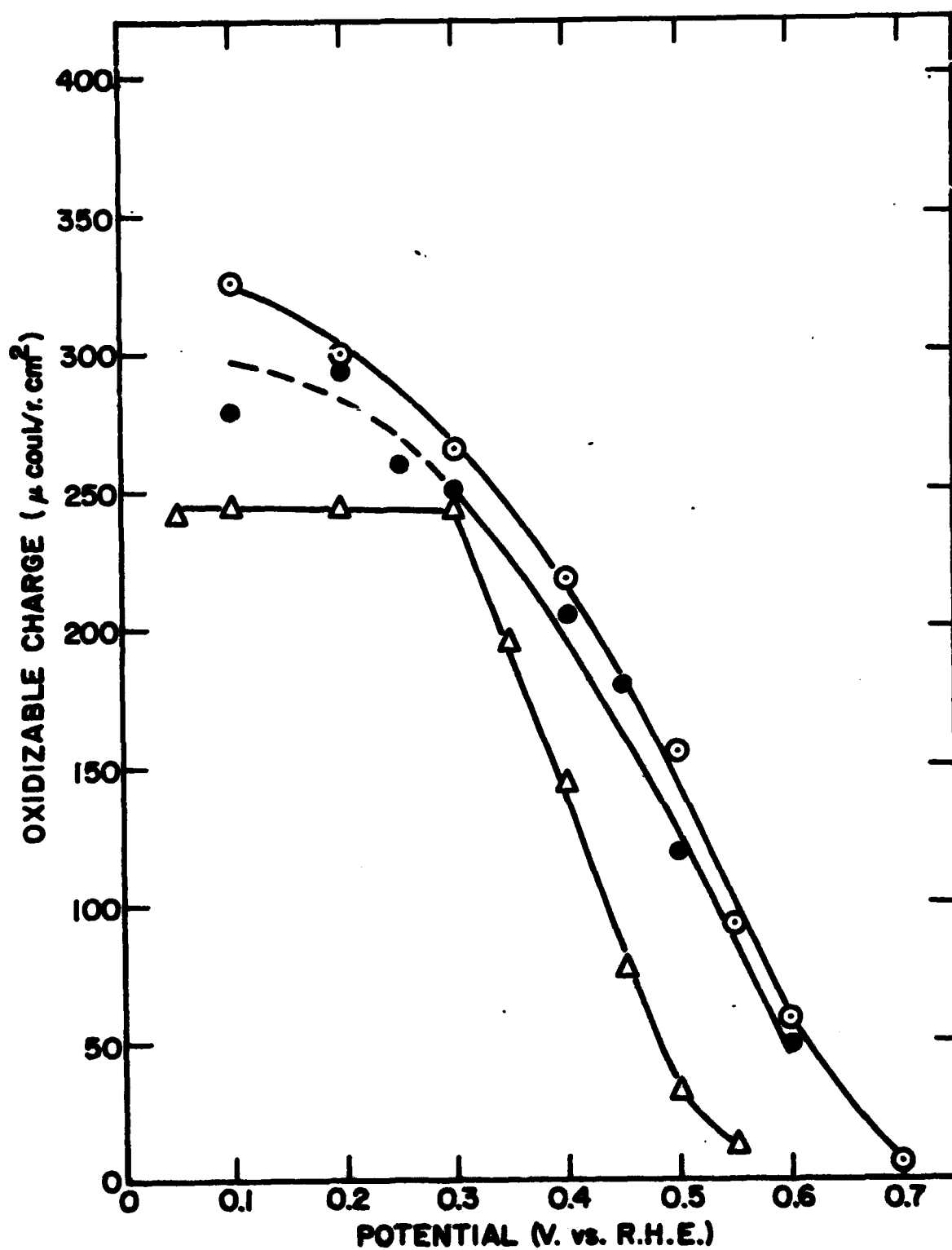


Fig. 6 Steady state adsorption at 130°C as a function of potential and material (○, Cu + CH<sub>4</sub>; ●, Cu; △, CH<sub>4</sub>).

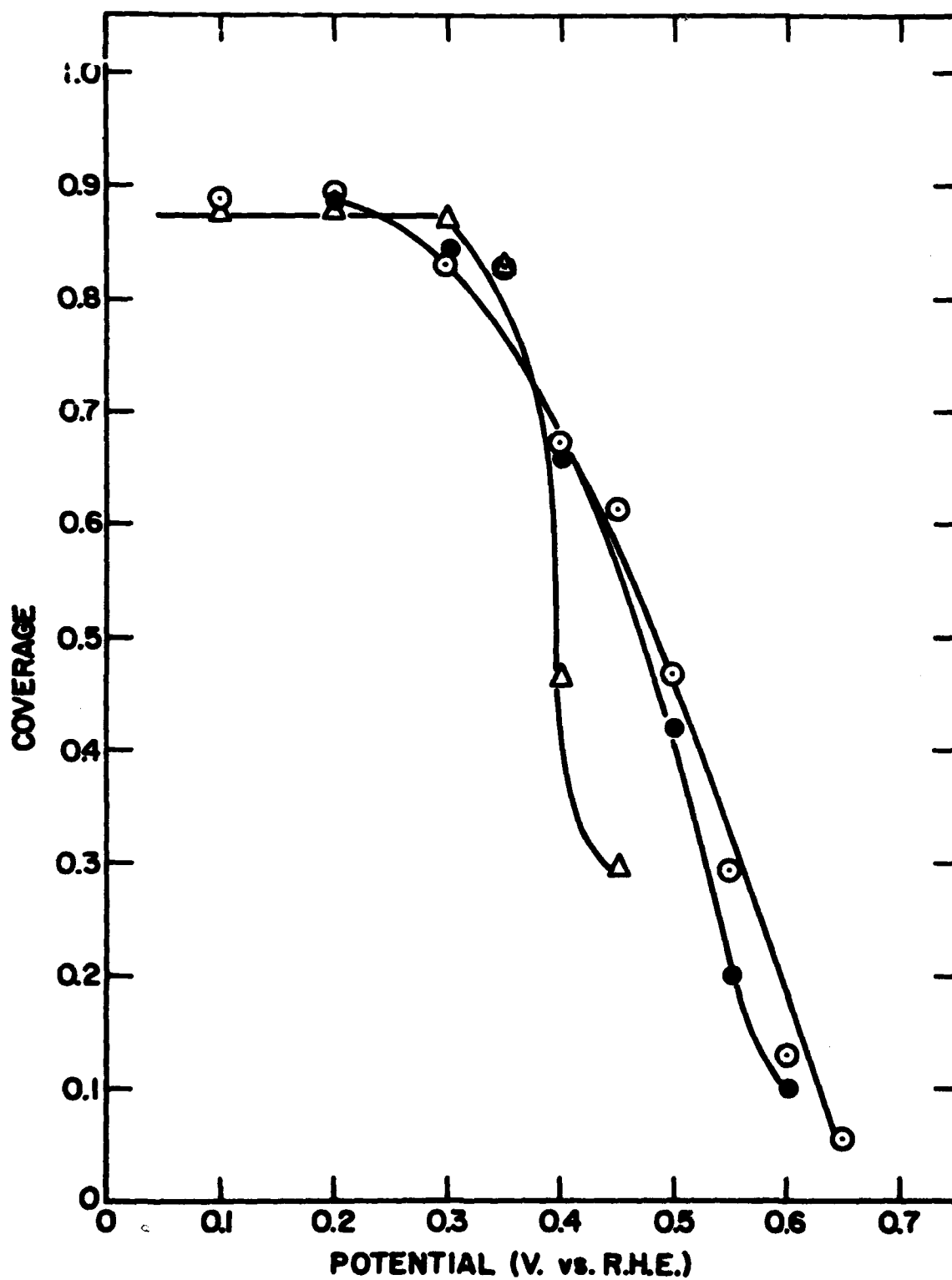


Fig. 7 Steady state coverages at 130°C as a function of potential and material (○, Cu + CH<sub>4</sub>; ●, Cu; △, CH<sub>4</sub>).

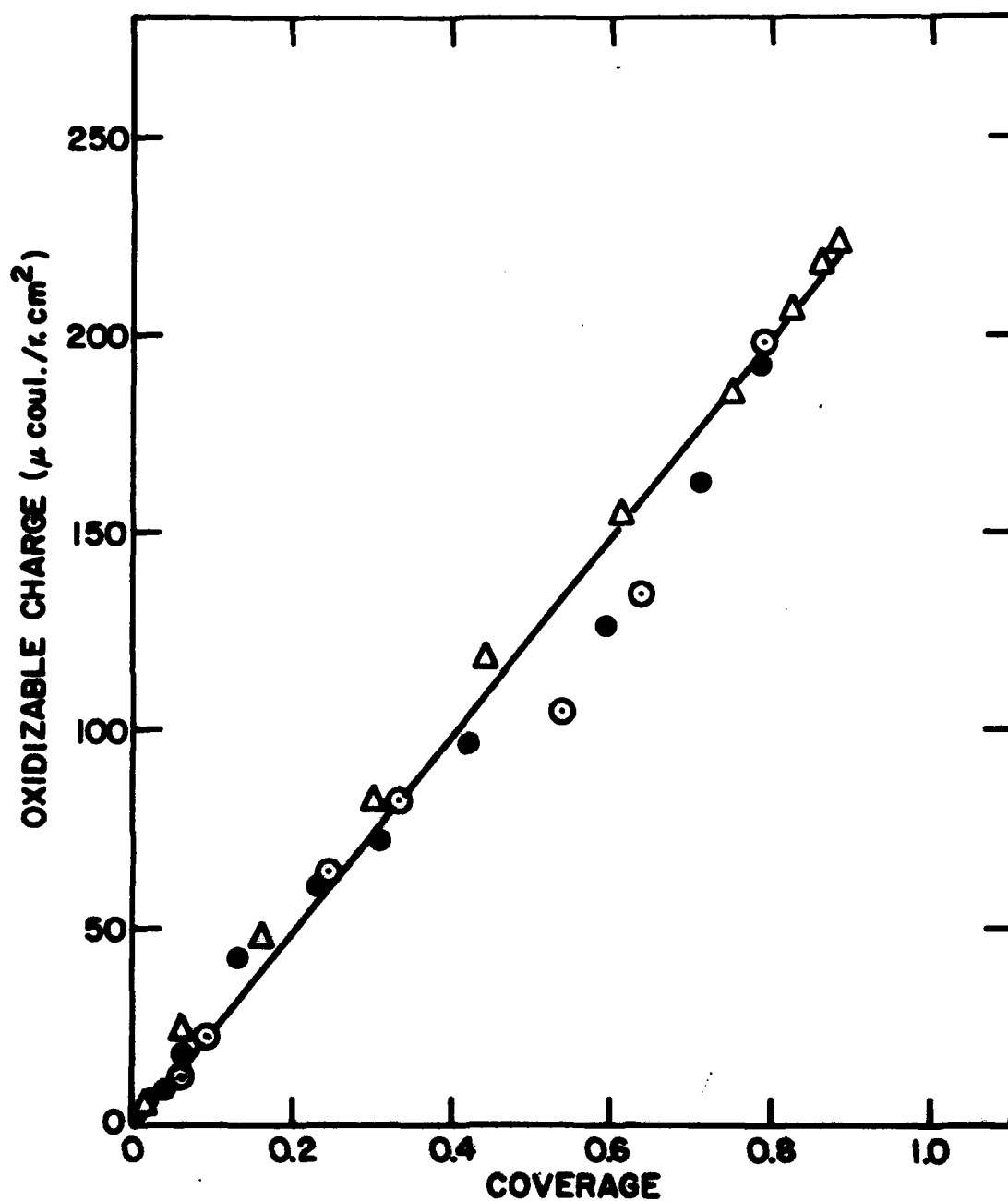


Fig. 8 A comparison of the ratios of charge accumulation to coverage of different materials adsorbed at 0.15 v and 130°C (○, Cu + CH<sub>4</sub>; ●, Cu; Δ, CH<sub>4</sub>).

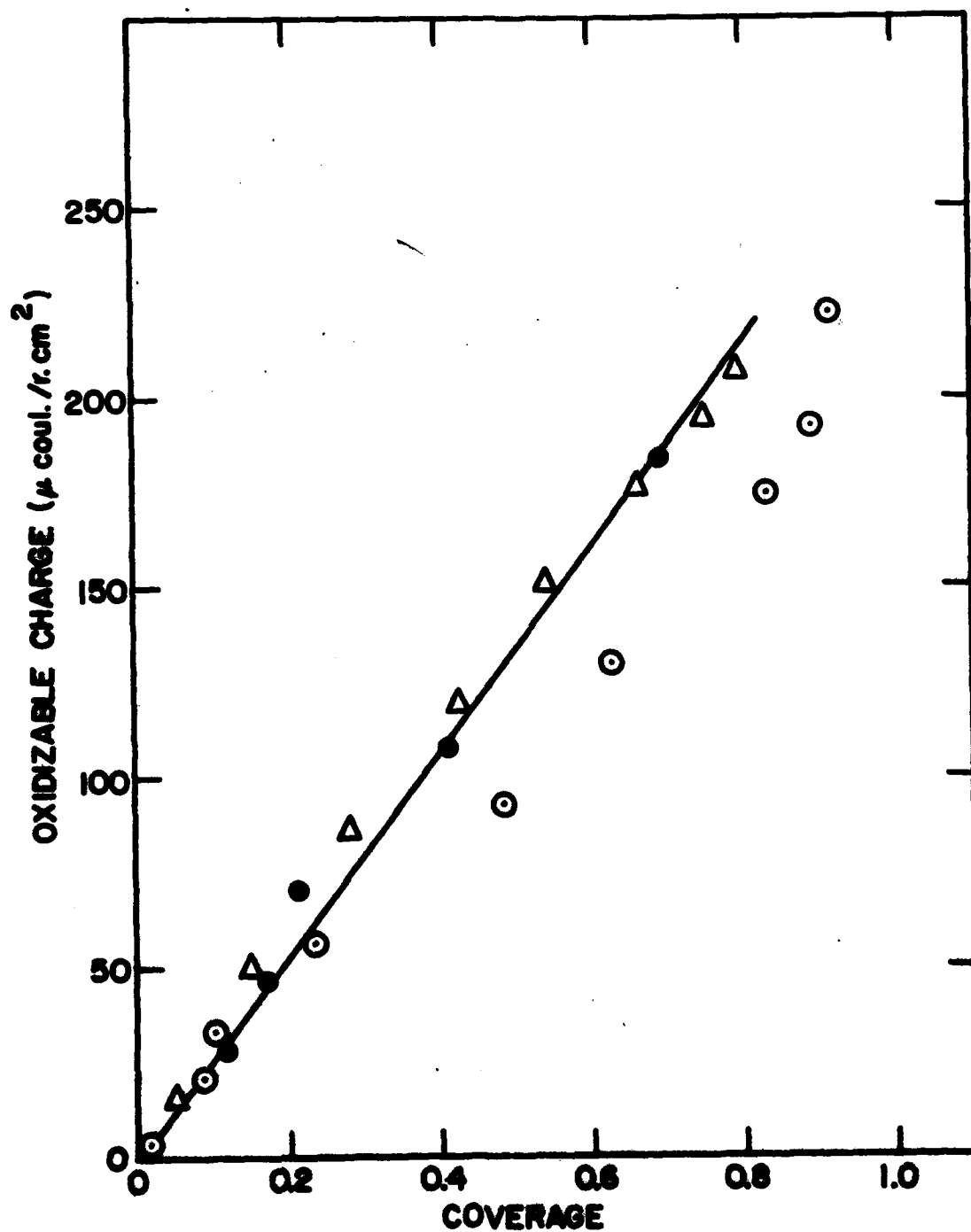


Fig. 9 A comparison of the ratios of charge accumulation to coverage of different materials adsorbed at 0.35 v and 130°C (●, Cu + CH<sub>4</sub>; ●, Cu; Δ, CH<sub>4</sub>).

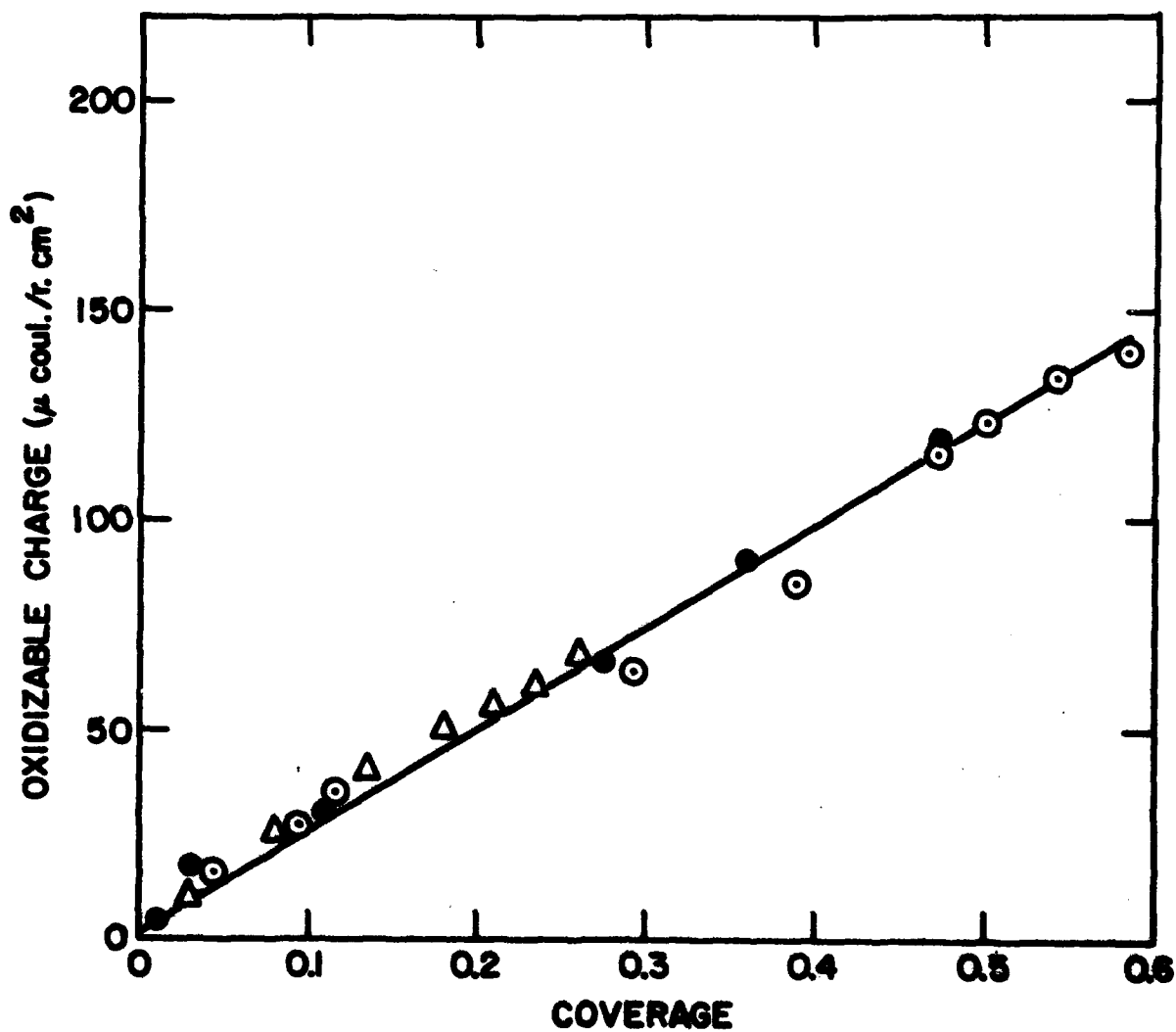


Fig. 10 A comparison of the ratios of charge accumulation to coverage of different materials adsorbed at 0.45 v and 130°C (○, Cu + CH<sub>4</sub>; ●, Cu; Δ, CH<sub>4</sub>).

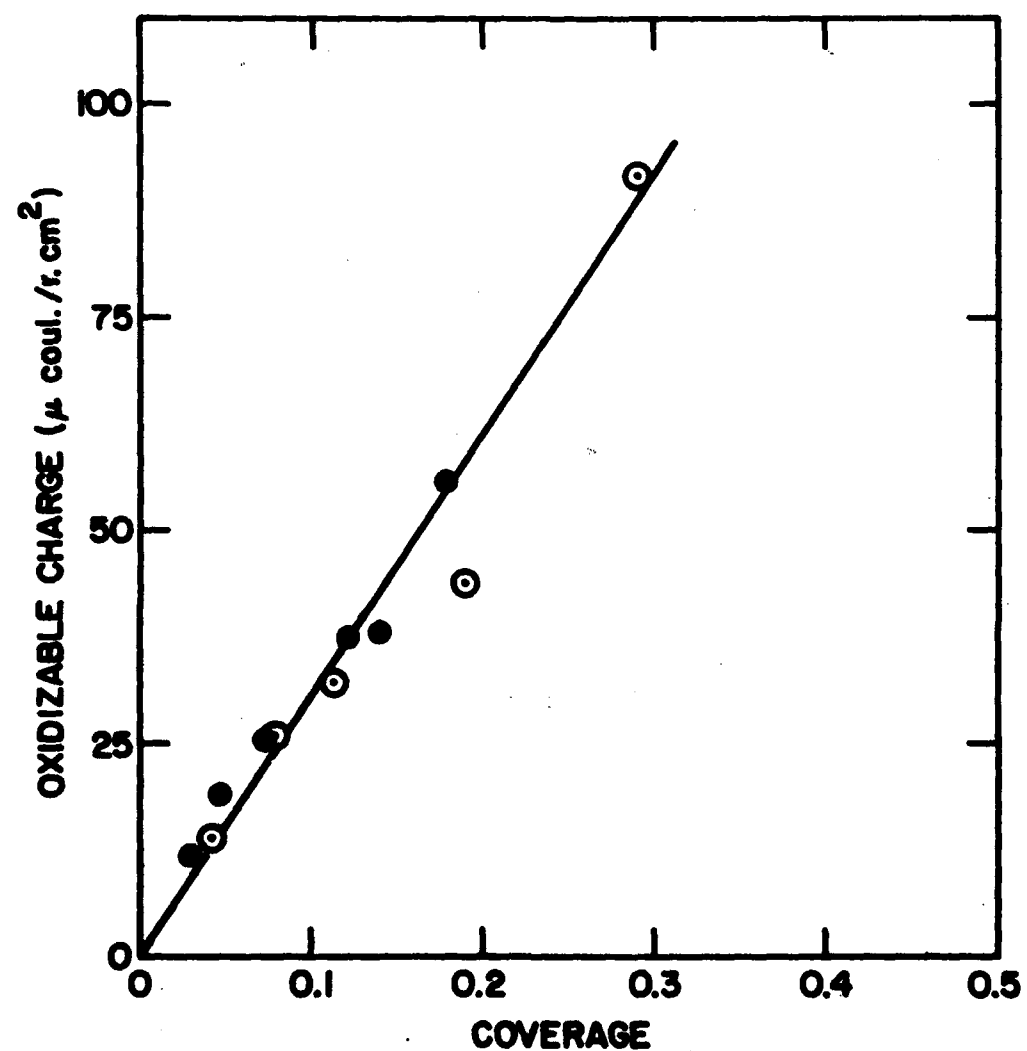


Fig. 11 A comparison of the ratios of charge accumulation to coverage of different materials adsorbed at 0.55 v and 130°C (○, Cu + CH<sub>4</sub>; ●, Cu).



are similar to those discussed in the previous section and in our last report, respectively. In this instance, we have fitted a line with a slope of about 1.2 electrons/site through the points. The difference between this value and the 1.05 electrons/site reported above is within experimental error for different determinations. As we have mentioned, the Cu and CH<sub>4</sub> layers are essentially identical over the whole potential range explored.

The combined Cu + CH<sub>4</sub> layer shows a minor difference, however. Thus, in the middle regions of coverage the charge to oxidize the layer does not appear to increase as rapidly as one would expect. Eventually, at higher coverages, the charge to oxidize the adsorbed layer increases more rapidly with coverage than expected and the total result is not very dissimilar to the results for the individual species. However, it is quite clear from the results that the Cu and CH<sub>4</sub> interfere with the mode of one another's adsorption in the intermediate coverage region. Even so, it is not possible from the results to distinguish which part of the combined adsorbate is Cu and which part is O-type CH<sub>4</sub>.

In our early experiments at 110°C it had appeared (see for example Fig. 3) that it would be quite easy to distinguish adsorbed Cu from adsorbed CH<sub>4</sub>, and indeed the experiments shown in Fig. 4 were only carried out after the results for Cu + CH<sub>4</sub> shown in Figs. 8 - 11 were available. The significance of being able to distinguish the co-adsorbed species is as follows: One would like to investigate the rate at which adsorbed CH<sub>4</sub> reacts in presence and in absence of Cu. Then, one is in a position to examine critically the catalytic behavior of an adsorbed inorganic layer on the over-all process. It is evident that no such distinguishing characteristic can be made from the Q - θ plots.

We should note that there are differences between the different adsorbed layers, although they are not very large. For example, we have already mentioned the minor differences between Cu and CH<sub>4</sub>, on the one hand, and their combined layer as far as

the  $Q - \theta$  plots are concerned. A similar, albeit minor, difference is seen in the average oxidation state of the adsorbed layer in the steady state (Fig. 12). We see that in general the layer is on average more reduced in the steady state than it is during the early stages of formation of the adsorbed layer. This, no doubt, corresponds to the presence of relatively small amounts of highly reduced species being produced during the latter stages of the formation of the layer. It is not possible to examine this latter process in detail during adsorption because of the difficulty of making accurate measurements of coverage when the electrode is almost completely covered. We see that the  $\text{Cu} + \text{CH}_4$  layer is on average slightly more reduced than the  $\text{Cu}$  layer or the  $\text{CH}_4$  layer. Probably the more highly reduced species in the presence of  $\text{Cu}^{++}$  is  $\text{Cu}$  adsorbed on one site and evidently at more positive potentials, where total coverage is in any case small, this is the major  $\text{Cu}$  species. Again we emphasize that although we can distinguish these small differences between the adsorbed layers, they are not useful in allowing a quantitative description of the components of the adsorbed layer.

A further effort to distinguish the components of the adsorbed layer was made from an examination of the potential decays when the circuit is opened after adsorption of the different species. Figure 13 shows typical behavior for a series of steady-state layers formed in presence of both  $\text{Cu}$  and  $\text{CH}_4$ . Results are shown for a range of potentials of adsorption from 0.15 to 0.55 v. The phenomena observed depend on the potential of adsorption. For adsorption below 0.4 v, the potential rises uniformly with time, finally settling to a value of about  $0.40 \pm 0.01$  v. For adsorption above 0.4 v, the potential at first drops rapidly and then subsequently rises again to about 0.4 v.

The results at 0.55 v were of particular interest and we explored the processes which were occurring during the potential decay. We found that the adsorbed layer grew during the decay. An attempt was made to analyze the changes on the electrode surface during this time, in order to examine the oxidation rate of O-type

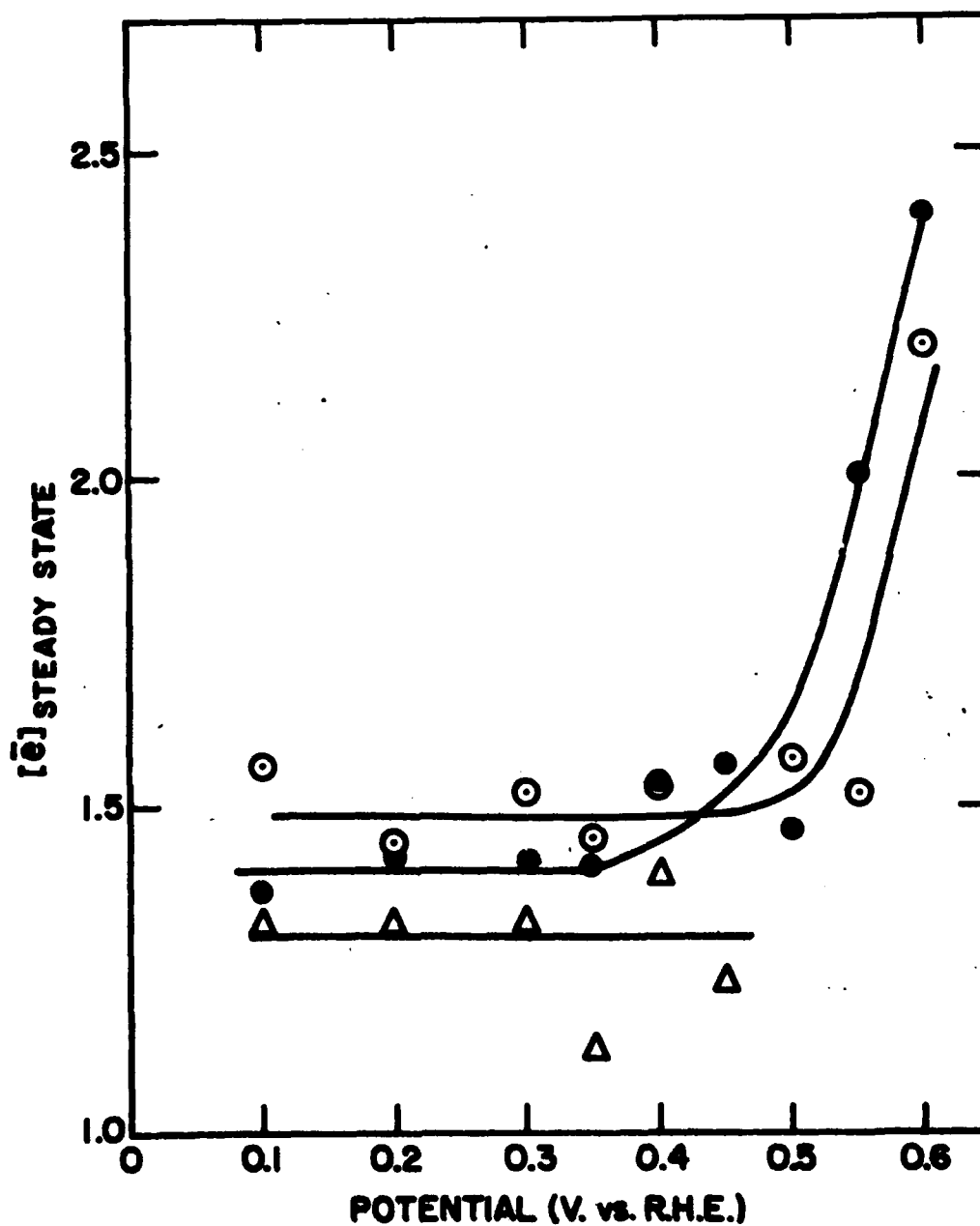


Fig. 12 Number of electrons required to oxidize the steady state adsorbate as a function of potential and material (○, Cu + CH<sub>4</sub>; ●, Cu; △, CH<sub>4</sub>).

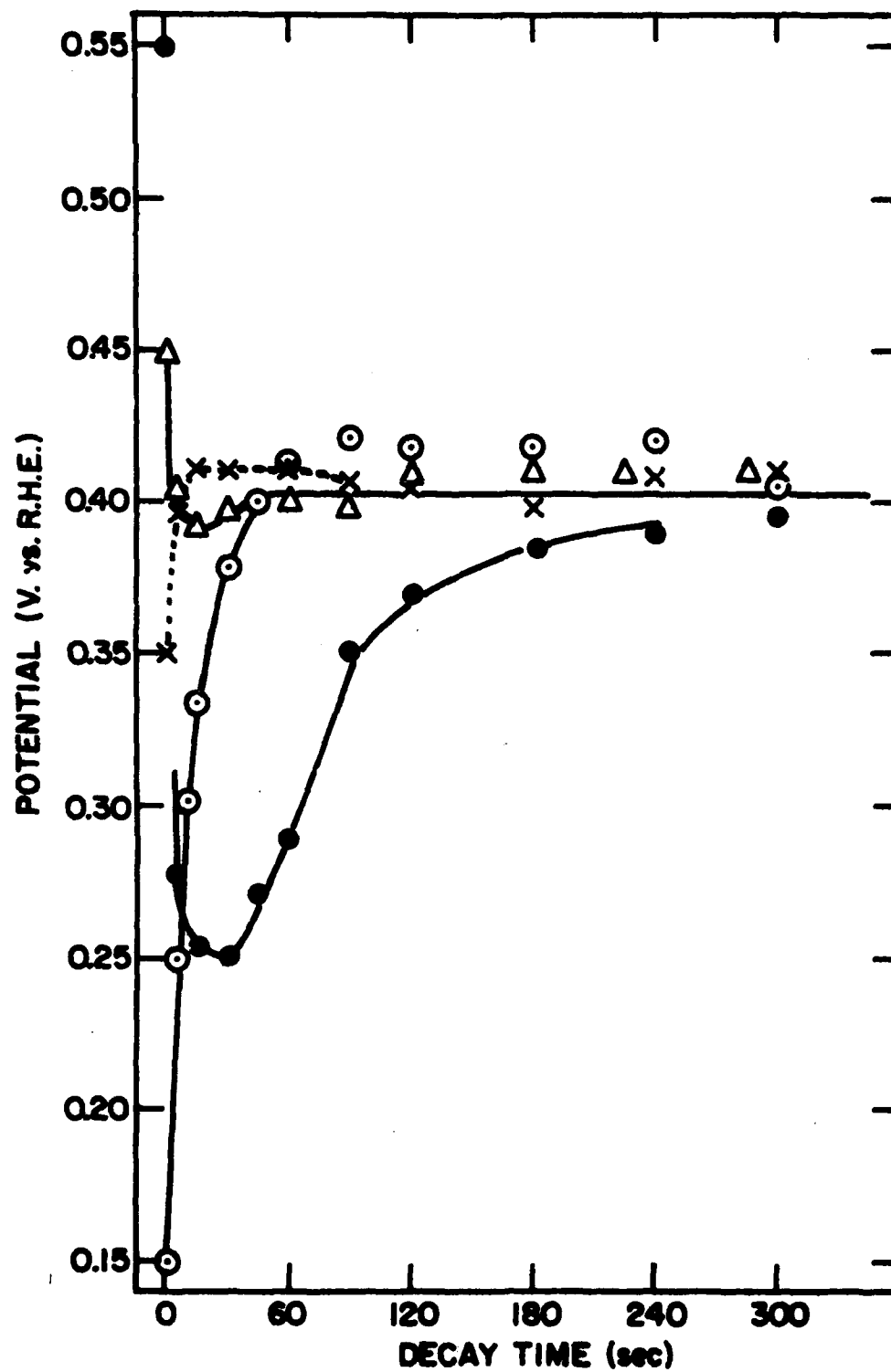
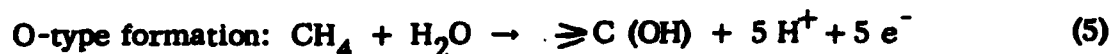


Fig. 13 Potential decay for Cu absorbates formed at different potentials (●, 0.15 v; X, 0.35 v; Δ, 0.45 v; ●, 0.55 v).

$\text{CH}_4$  in presence of Cu. The following processes were considered:



In particular we were interested in reaction (6). Due to the similarities of oxidation state of the various adsorbed layers, we were unable to resolve the component rates of these processes. In early results, where we had believed following Fig. 3 that the oxidation state of Cu was quite different from that of  $\text{CH}_4$ , there were some indications that O-type oxidation is enhanced by presence of Cu. However, at this time, we do not believe that a quantitative interpretation of the potential decay after adsorption is appropriate.

Qualitatively, however, we can see a significant difference in behavior between the case of Cu and the case of  $(\text{Cu} + \text{CH}_4)$ . Figure 14 compares potential decays for these situations for adsorbates formed at 0.15 and 0.45 v. We see that in presence of only Cu the potential rises uniformly with a sloping arrest in the region of 0.55 v. Eventually, the electrode potential rises to about 0.94 v. In presence of both Cu and  $\text{CH}_4$ , the decays are as described previously and they terminate quite rapidly at about 0.40 v. These are sharp differences in behavior, but again, they do allow us to resolve the components of the adsorbed layer quantitatively.

These experiments do not seem able to resolve the structure of the adsorbed layers on smooth Pt. To do this, we have recently designed a cell in which it will be possible to absorb Cu to a known coverage in one compartment and then to study the properties of this layer in catalyzing  $\text{CH}_4$  oxidation in another compartment. This system is a container in which the working electrode can be transferred between each of two self-contained electrochemical cells. It will allow a

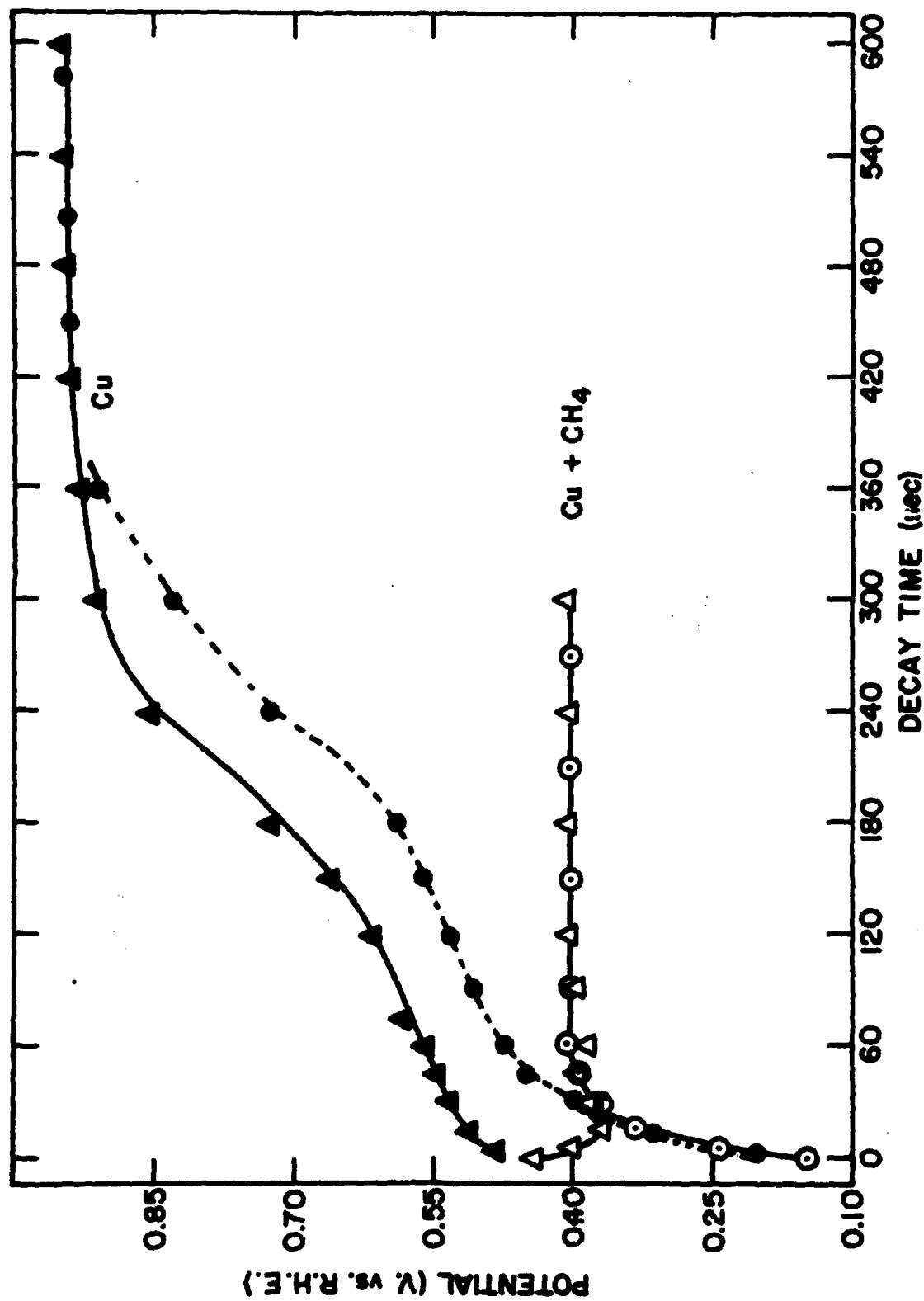


Fig. 14 Comparison of potential decays for Cu and Cu + CH<sub>4</sub> layers (○, 0.15 v and Δ, 0.45 v for Cu + CH<sub>4</sub>; ●, 0.15 v; ▲, 0.45 v for Cu).

complete resolution of the properties of adsorbed organic layers in presence of inorganic layers since they will each be separately established. In addition, we have carried out some less complex but nevertheless revealing experiments with platinized electrodes in our conventional cell.

## V. CO-ADSORPTION OF Cu AND CH<sub>4</sub> ON PLATINIZED Pt

Figure 15 shows the steady state adsorbate charge for CH<sub>4</sub> and Cu + CH<sub>4</sub> on platinized Pt electrode. We see considerably greater adsorption for the combined layer and undoubtedly most, if not at all, of this is Cu.

In Fig. 16 we show the relation between the steady-state current for CH<sub>4</sub> oxidation and the potential with different amounts of Cu<sup>++</sup> in solution. We observe that even minor amounts of Cu<sup>++</sup> inhibit the oxidation of CH<sub>4</sub>. Thus, notable effects are seen with addition of as little as 2  $\mu$ M Cu<sup>++</sup>, i.e. 60 parts per billion! The effect of higher concentrations of Cu<sup>++</sup> seems to be a strong inhibition. This is shown in more detail in Fig. 17, where we show the oxidation rate for CH<sub>4</sub> as a direct function of Cu concentration at various potentials. We see that in general the first increments of Cu<sup>++</sup> in solution are the most deleterious. This presumably reflects the isotherm for adsorption of Cu.

The experiments described here indicate that adsorbed Cu inhibits the over-all CH<sub>4</sub> to CO<sub>2</sub> reaction. However, we are also particularly concerned with trying to decide whether the adsorbed inorganic layer can catalyze the oxidation of O-type to CO<sub>2</sub>. If this were the case, and if at the same time the adsorbed inorganic species inhibited the adsorption step in the CH<sub>4</sub> to CO<sub>2</sub> reaction, the net effect would be inhibition of the over-all process. However, the finding of a catalyst for O-type oxidation, i. e. reaction (6), would be a big step towards evolving a multicomponent polyfunctional adsorbed catalyst. Correspondingly, we have explored the rate of O-type oxidation on platinized Pt in presence of adsorbed Cu.

The experiment was as follows: The steady state adsorbed layer was formed at 0.30 v vs. RHE. The electrode potential was then lowered to 0.20 v for 10 minutes, while CH<sub>4</sub> was flushed from the system with N<sub>2</sub>. Then the electrode potential was returned to 0.30 v for one minute without stirring. The adsorbed layer was then



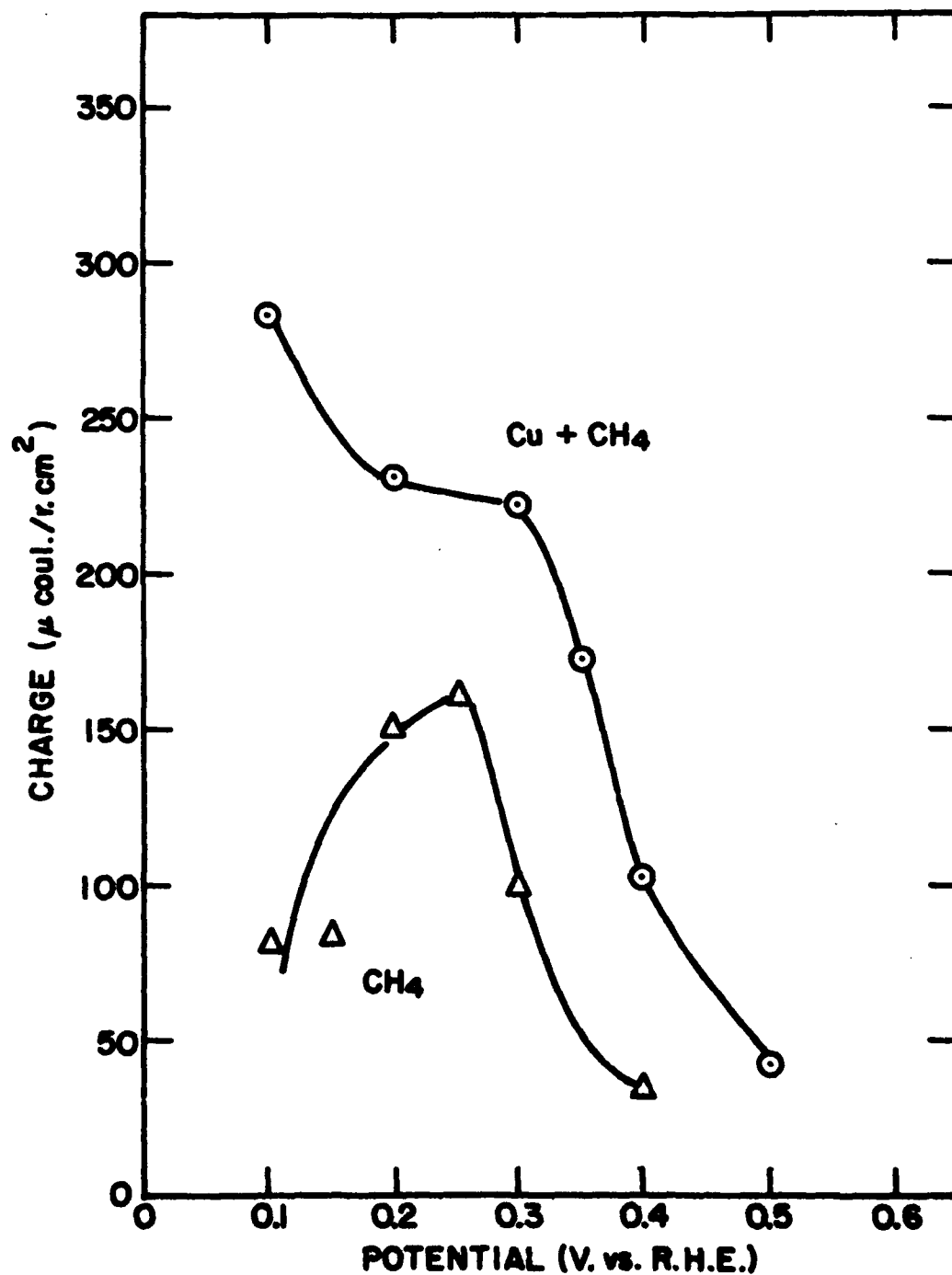


Fig. 15 Steady state adsorption on platinized Pt as a function of potential.

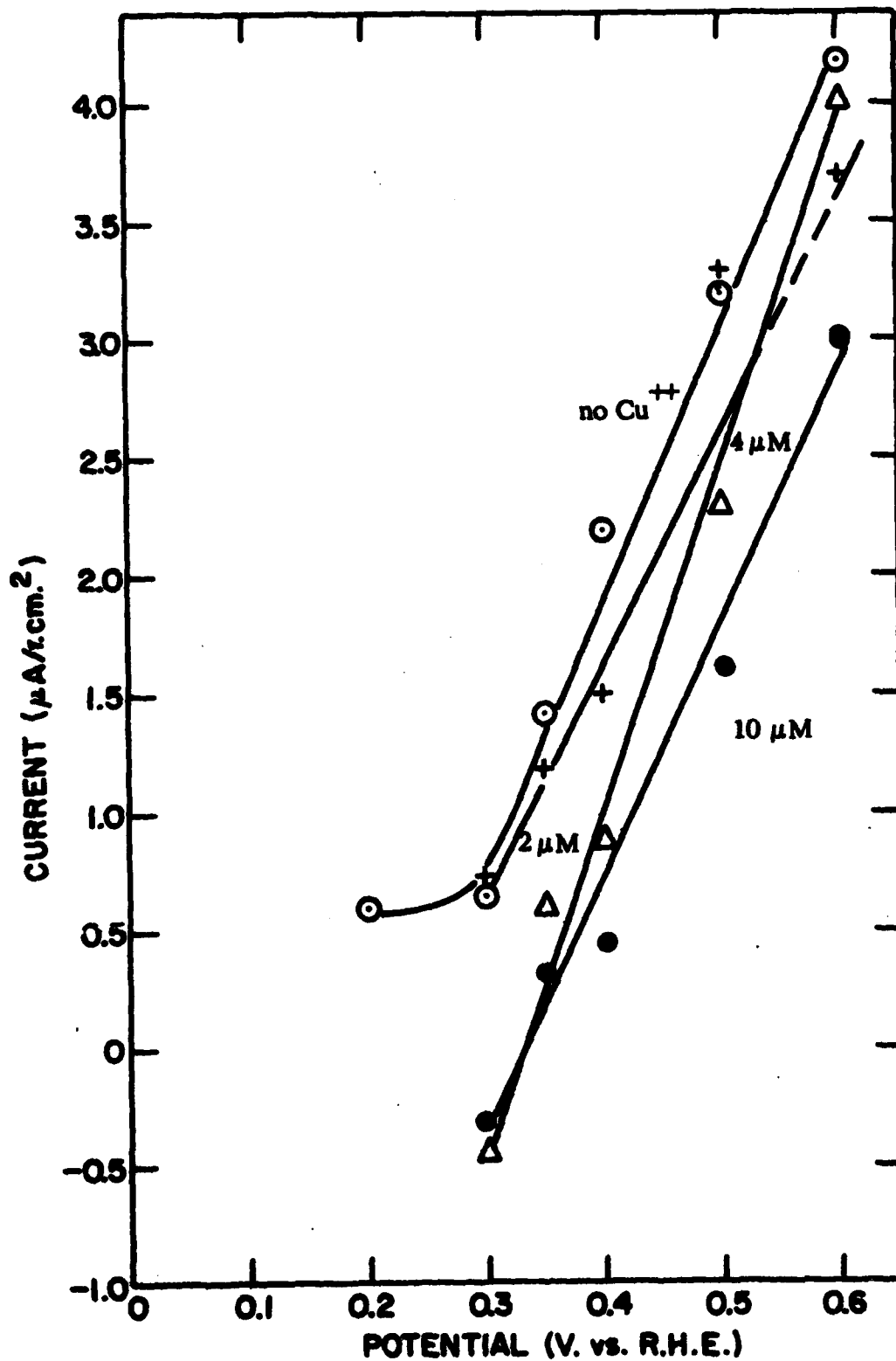


Fig. 16 Current for  $\text{CH}_4$  oxidation as a function of potential and concentration of a  $\text{Cu}^{++}$  in solution.

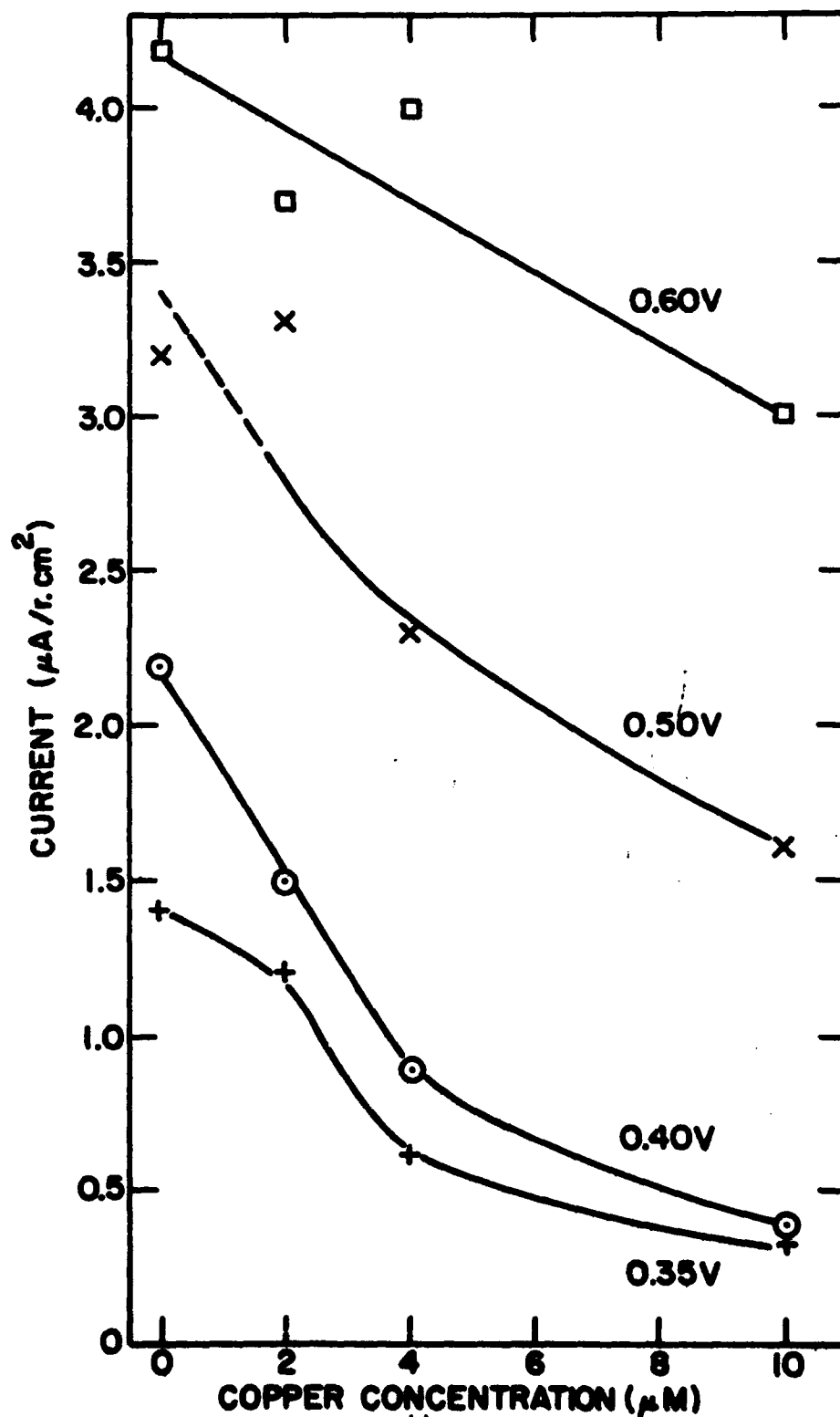


Fig. 17 Current as a function of  $\text{Cu}^{++}$  concentration at various potentials.

stripped off by means of a small anodic current. It turned out that the adsorbed  $\text{CH}_4$  started to oxidize before the adsorbed Cu. Correspondingly, we could determine the potential at a given current corresponding to the initial oxidation of O-type  $\text{CH}_4$  in presence of adsorbed Cu. This is similar to the experiments we have described previously for adsorbed  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$ . The results are shown in Fig. 18. Here, we have compared the current potential curves for the initial oxidation of O-type  $\text{CH}_4$  in absence and in presence of adsorbed Cu. The results for O-type  $\text{CH}_4$  are from our last report. We see a similar Tafel relationship in presence as in absence of Cu, i. e. approximately  $1.5 \text{ RT/F}$ . However, at any potential, the rate of oxidation of O-type  $\text{CH}_4$  is lower in presence of Cu than in absence; i. e. the Cu, when adsorbed, does inhibit the rate of O-type electro-oxidation.

We feel that the techniques described in this section will be particularly useful for screening different inorganic adsorbed layers prior to making more intensive studies of those systems which turn out to be promising. The more intensive studies would be done with our newly designed cell.

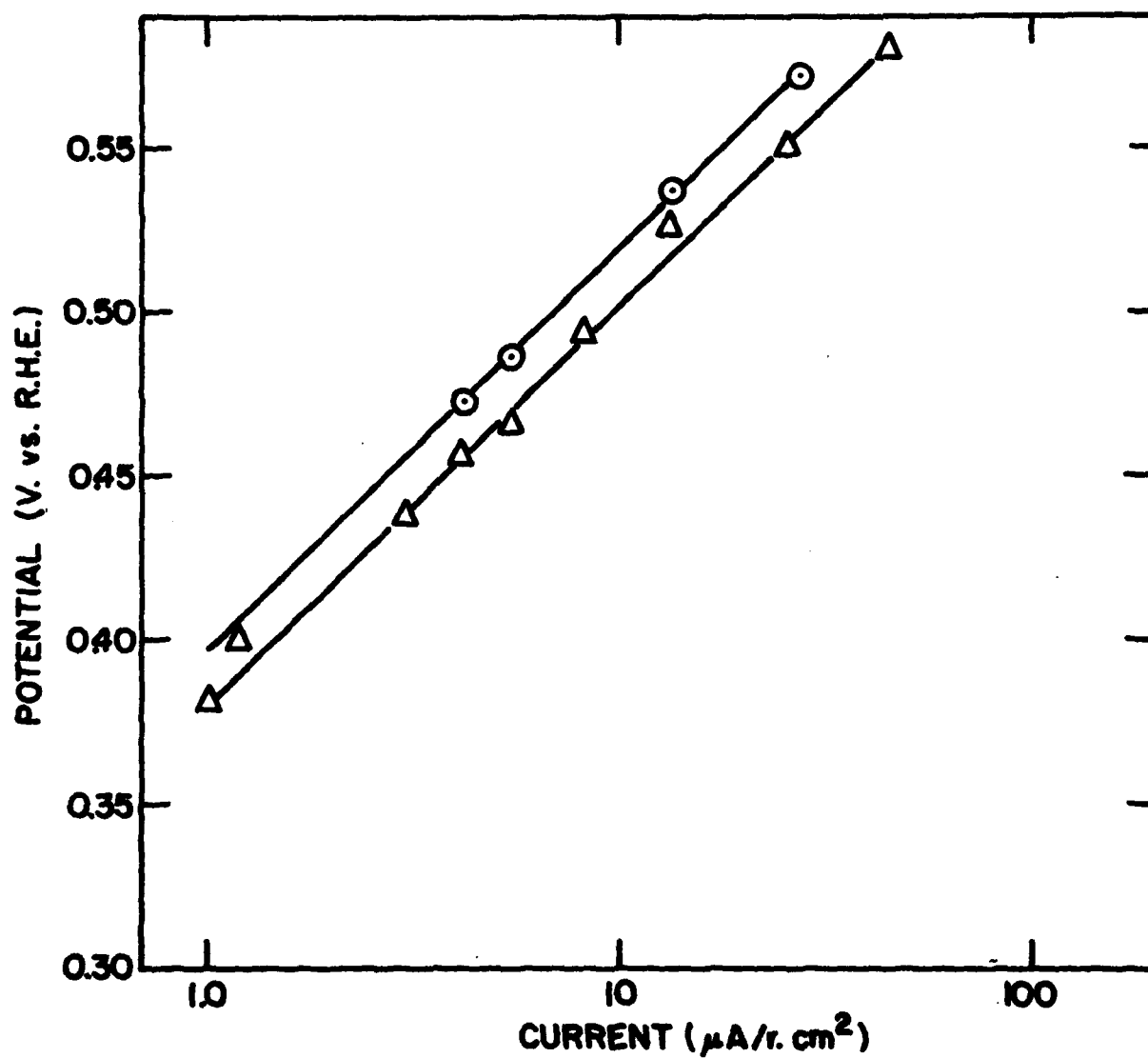


Fig. 18 Initial oxidation potential of adsorbates formed at 0.30 v as a function of stripping current density ( $\Delta$ ,  $\text{CH}_4$ ;  $\odot$ ,  $\text{Cu} + \text{CH}_4$ ).

## VI. SUMMARY AND FUTURE WORK

We have seen that it is possible to adsorb submonolayer quantities of Cu on both smooth and platinized Pt in our hot concentrated  $\text{H}_3\text{PO}_4$  solution. We are hopeful, therefore, that the principle of adsorption stabilized nonmetal catalysts may be fairly general. Further exploratory studies using other heavy metal ions, e.g.  $\text{Ni}^{++}$  and  $\text{Fe}^{++}$ , will be correspondingly undertaken.

Studies will be made initially with platinized Pt in the manner described for Cu in section V of this report, and more detailed investigations of some systems will be carried out in our newly designed cell.

The results to date show that Cu inhibits the over-all  $\text{CH}_4$  to  $\text{CO}_2$  reaction and that it does so by inhibiting the rate of the limiting step, i. e. O-type oxidation. Some minor further investigation of this system is required to establish whether the inhibition of the over-all process is quantitatively the result of the inhibition of O-type oxidation. It may be that adsorbed Cu also inhibits to some extent the initial adsorption process. If this is the case we expect to find a lowering of the coverage of the surface with O-type.

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1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION
Tyco Laboratories, Inc. Waltham, Massachusetts 02154		2b. GROUP
3. REPORT TITLE		
RESEARCH ON THE ELECTROCHEMICAL OXIDATION OF HEXANE AND ITS ISOMERS		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
Sixth Semiannual Interim Report (May 16 - November 15, 1968)		
5. AUTHOR(S) (Last name, first name, initial)		
Brummer, S. B. Turner, M. J.		
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
	39	29
8a. CONTRACT OR GRANT NO.		8a. ORIGINATOR'S REPORT NUMBER(S)
DA 44-009-AMC-1408(T)		
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13. ABSTRACT		
<p>The oxidation of <math>\text{CH}_4</math> on Pt electrodes in 80% <math>\text{H}_3\text{PO}_4</math> has been studied at 110 and 130°C. Particular emphasis has been placed on possible methods of developing non-noble metal catalysts. The difficulties associated with this development, in particular corrosion, are discussed. A possible method of overcoming these difficulties and of stabilizing non-noble methods is described, involving their adsorption in submonolayer quantities.</p> <p>A study of Cu adsorbed on both smooth and platinized Pt has been made. In presence of <math>\text{Cu}^{++}</math>, Cu is adsorbed onto Pt at a rate limited by <math>\text{Cu}^{++}</math> diffusion. Steady-state coverage is high and the isotherm is very similar to isotherms found for typical organic species; there is high coverage at low potentials (<math>\leq 0.3</math> v vs. RHE) and a decrease in coverage at higher potentials. The coverage becomes zero above 0.7 v. The relationship between the charge to oxidize the Cu layer, Q, and its coverage, <math>\theta</math>, allows calculation of the number of electrons released per site when the layer is oxidized, [e]. For Cu at 130°C, [e] is 1 electron/site, i.e. indistinguishable from O-type hydrocarbons. An [e] value of 1</p>		

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### 13. Abstract (cont'd.)

electron/site would correspond to a layer where the Cu atoms occupy two Pt surface sites. At 110°C the Cu layer releases about 1.8 electrons/site on oxidation, indicating that each Cu atom occupies one Pt site.

→ Cu adsorbs less rapidly in presence of  $\text{CH}_4$ , than in its absence. The evidence for this is that while the rate of adsorption of the combined layer, in presence of both  $\text{CH}_4$  and  $\text{Cu}^{++}$ , is higher than in presence of either  $\text{CH}_4$  or  $\text{Cu}^{++}$  alone, it is slower than the sum of the rates of adsorption of the two components. In the steady state, both the coverage and the charge to oxidize the adsorbed layer are higher in presence of both  $\text{Cu}^{++}$  and  $\text{CH}_4$  than in presence of either component alone. However, coverage or charge is lower than their respective sums for Cu and  $\text{CH}_4$  alone.

The charge vs. coverage plots in presence of adsorbed Cu and  $\text{CH}_4$  are slightly different than for the individual components; in the middle range of coverage the plot for the combined layer departs from linearity and invariably shows less oxidizable charge than anticipated. There is also a slight difference in the average oxidation state of the various adsorbed layers in the steady state. Thus, for adsorption at potentials below 0.4v,  $\text{CH}_4$  releases about 1.25 electrons/site on oxidation and the combined layer releases about 1.4 electrons/site. Above 0.4v, both the Cu and the Cu +  $\text{CH}_4$  layers show a sharp increase in the average oxidation state of the adsorbed layer.

There is a distinct difference in behavior between Cu and the Cu +  $\text{CH}_4$  combined layer with respect to behavior on open circuit after formation. When an electrode with a Cu layer is open circuited, its potential rises to about 0.94 v with a sloping arrest in the region of 0.55 v. The behavior of an electrode with a Cu +  $\text{CH}_4$  layer depends on its potential of formation. In all cases the final potential is  $0.40 \pm 0.01$  v. For adsorption above 0.4 v, the potential first moves to lower values, during which increasing adsorption occurs at open circuit. For adsorption potentials below 0.4 v, there is a uniform increase to 0.4 v on open circuit. The shapes of these transients are determined by equal anodic and cathodic reactions involving  $\text{Cu}^{++}$  deposition and O-type  $\text{CH}_4$  formation and oxidation.

13. Abstract (cont'd.)

A quantitative analysis of the contributions of these individual reactions is not possible, however, and a special cell is described in which it is possible to form the inorganic and organic layers separately and quantitatively and to study the effects of the inorganic layer on the properties of the adsorbed layer.

→ On platinized Pt the charge to oxidize the combined  $\text{Cu} + \text{CH}_4$  layer is considerably greater than the corresponding charge for pure  $\text{CH}_4$ . The over-all oxidation rate of  $\text{CH}_4$  is inhibited in presence of  $\text{Cu}^{++}$  and concentrations of  $\text{Cu}^{++}$  as low as 60 parts per billion significantly decrease the hydrocarbon oxidation rate. It is shown that this inhibition arises substantially from the inhibition of the rate-limiting step of the  $\text{CH}_4$  oxidation reaction, i. e. the oxidation of O-type to  $\text{CO}_2$ . <

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